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THE WASTE AND CONSERVATION OF PLANT FOOD.[1]

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ONE of the greatest of the practical problems presented for solution by agricultural chemistry is the conservation of plant food. With an abundance of plant food and a favoring climate, it is difficult to place a limit to the power of the earth for supporting life. We have read much in political economy of the limit of subsistence, and one bold philosopher has based a theory of the limitation of the number of human beings upon the earth on the insufficiency of the earth to support a greater number. Happily, however, the Malthusian philosophy was promulgated before the days of that great agricultural renaissance which has been brought about chiefly through the efforts of experimental agricultural chemistry. I am not so blinded by the achievements of agricultural chemistry as to deny to many other branches of science an important and, in many cases, necessary influence in this development of agricultural science; but I think every candid man will admit that in this development chemistry has always taken the front rank and led the way. This is pre-eminently true of the investigations into the nature and extent of the plant food available on the surface of the earth. In this country, owing to the great stores of wealth which the past had accumulated in the soil, it is only within recent years that the question of the supply of plant food has assumed any practical importance. As long as there

[1]Retiring address of the President of the American Chemical Society, Baltimore Meeting, December 27, 1893.

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were virgin fields at the disposal of the agricultural rapist, the conservation and restoration of exhausted fields was of little consequence. The result has been that the wealth of hundreds or, perhaps, thousands of years slowly stored in the soil has been poured forth in a century, not only for the enrichment of this country, but for the benefit of all countries. Unfortunately, or fortunately, these stores are now practically explored and there is little left in this land of virgin fertility to tempt the farmer to new conquests. Not only have these stores of plant food been utilized, but, much to the discredit of the American farmer, they have been wasted. The mark of good agriculture is to see fields yielding annually good returns and increasing, or at least not lessening in fertility. This being true, the history of American agriculture to within a few years must be the history of bad farming, for everywhere we have seen fertile fields losing their fertility and farms once productive abandoned. No difference how great the store may be, if it be continually drawn upon and never replenished, the day will some time come when it will be exhausted. This day has come to a large portion of the agricultural lands of this country, and to-day there is an awakening everywhere in regard to the best methods of checking the waste and of restoring what has been lost.

I desire for a brief period, on this occasion, to call the attention of the chemists of this country to some of the methods by which plant food is removed from the fields and some of the direct and indirect ways in which it is and may be returned. On a former occasion[1] I have discussed the extent to which plant food is removed from the soil directly in the crops and the dangers which arise to an agricultural community which continually exports its agricultural products. On that occasion I pointed out the amount of potash, phosphoric acid, and nitrogen per acre annually removed by the crops of the United States, and showed that the only safe agricultural products to send out of a country were sugar, oil, and cotton. It is true that with native, unexhausted soils a country may acquire great wealth by agricultural exports, but the history of the world shows that a

[1]Vice Presidential Address before the American Association for the Advancement of Science, Buffalo, 1886.

country which depends for its wealth and its commerce on agricultural exportation is in the end reduced to pauperism. A single example may serve to accentuate this remark; I refer to the island of Cyprus, which two thousand years ago was the granary of many cities bordering on the Mediterranean Sea. Supplying hundreds of thousands of people with corn, it gradually became impoverished, and to-day its soils are perhaps the poorest of any known.

The waste to which I desire to call your attention to-day is not that which normally takes place in the production of a crop, but that which is incidental to the cultivation of the soil and to a certain extent unavoidable. My purpose is to develop, if it be possible, the relations of agricultural chemistry to this waste, with the purpose of pointing out a course by which it can be returned and in what way we may at least reduce to a minimum the unavoidable removal of valuable plant food. You have all, perhaps, surmised the character of this waste; I refer to the denudation of fields by water and to the removal of soluble plant food by the percolation of water through the soil.

The losses due to the denudation of fields are purely of a mechanical character. The natural forest, or the natural covering of grass over an area of soil, prevents, to a large extent, the denudation due to heavy downpours of rain. The removal of the forest, and the destruction of the grass by cultivation, leave the soil in a condition in which it is unable to resist the action of flowing surface water. The muddy character of the water in all streams bordering on cultivated hilly fields after a heavy rain storm is a familiar instance of the tremendous energies which are exerted by a heavy downpour of rain in the carrying of the soil into the streams and its transportation towards the sea.

It is not necessary to emphasize the fact that the agricultural chemist is practically powerless to prevent the surface erosion due to heavy rains, but a few practical lessons derived from the application of chemical discoveries to the soils show how, in a certain measure, even surface erosion may be controlled, or at least reduced to a minimum by the application of the principles

of culture founded upon the facts disclosed by advanced science.

The observing agriculturist will have noticed that even in a hilly country a soil *in situ* underlaid by limestone is less likely to be cut up by gullies than a soil similarly situated and deficient in carbonate of lime. The reason of this is plain. In a soil deficient in lime the clays when once brought into suspension by moving water assume a semi-colloid state and remain indefinitely in suspension. Clays, on the other hand, which are heavily impregnated with lime salts are in a flocculated state, and the larger aggregates thus produced settle quickly. The result of this is that such a soil is less easily moved by water, and a field thus treated less exposed to washing by heavy rains.

Our knowledge of flocculation and its physical and chemical results is due largely to the investigations of Shulze, Schloesing, and Hilgard, and the results of their researches have shown in a most emphatic way the beneficial changes which take place, especially in stiff clay soils, by the application of lime.

It is thus an incontrovertible fact that the surface washing of cultivated fields, especially if they be naturally deficient in lime, could be greatly diminished and has been greatly diminished by the free application of this substance.

The change in the physical condition of the soil, which is produced by the lime, is also another important factor worthy of consideration. A stiff clay soil is almost impervious to the penetration of surface water and thus the amount which is carried off is raised to a maximum. A well-limed soil, on the contrary, in which the particles are perfectly flocculated, is much more pervious and the amount of water which will be retained and delivered gradually to vegetable growth is much greater. Thus the beneficial effects of lime are manifested in both ways; in the better retention of the flocculated clays and in increasing the capacity of the soil for holding a given amount of water in its interstitial spaces.

There are many other salts which also have the same properties as those of lime, but I have spoken of lime salts chiefly because they are cheaper and, therefore, more economically applied. Perhaps next to lime, common salt would be the most

efficient in producing the results already described; but common salt being extremely soluble would soon be leached out of a soil. On the other hand, lime, even when supplied as hydrate, in which case it is somewhat soluble, quickly becomes converted into a carbonate which is practically insoluble in water which does not contain an excess of carbon dioxide.

I am aware of the fact that liming to prevent erosion by surface drainage has not been emphasized as an example of the benefit of the proper chemical treatment of soils, yet I feel sure that all who will give the subject a thoughtful consideration will agree with me in saying that this aspect of the subject is one of no small importance, especially when considered in respect of hilly fields, and even of fields of more level surface.

Without dwelling long upon this point, it is only necessary to call your attention to the immense quantities of soil material annually conveyed to the sea by the causes of erosion already mentioned to show what an active and powerful foe the farmer has in this source of loss. Anyone who watches, even for a short time, the volume of water carried by the Mississippi into the Gulf of Mexico will have a most effective object lesson in regard to this source of loss.

A more striking lesson may be seen in the hill regions bordering both banks of the Ohio river. Hundreds of fields once covered with sturdy forests of oak, maple, and walnut, and afterwards bearing large crops of maize, tobacco, and wheat, may now be seen furrowed with gullies, as with the wrinkles of age, and abandoned to brush and briars. The same is doubtless true of other hill regions, but I speak the more advisedly of those which have come under my personal observation.

Great, however, as the mechanical loss of plant food is, it is by no means as dangerous as the loss of the soluble materials caused by the percolation of the water through the soil. The study of the nature of the loss of these soluble materials, together with the estimation of their amount, forms the subject of lysimetry. Agricultural chemists have used many devices for the purpose of determining the character and amount of the natural drainage of soils. Evidently the treatment of a specially prepared portion of soil by any solvent, although giving in-

teresting results, does not indicate the natural course of solution. The only way in which this can be determined is to be able to collect, measure and study the character of the drainage from a given portion of the arable surface of the earth *in situ* and under normal conditions. Various methods of lysimetric investigation have been proposed and used, all of them possessing many points of value.

An excellent system of such observation has been established, for instance, at the Agricultural Experiment Station of Indiana. It is not my purpose, however, to discuss the mechanical details of lysimetry, but only to call your attention to the main principles which underlie it. The movement of water near the earth's surface is a matter of especial interest to agriculturists. Whitney[1] has clearly pointed out that the little excess or deficiency of water is of far more importance to the growing crop than the quantity of the excess or deficiency of its other foods. Soils richest in plant food will produce a small harvest if there be a great excess or deficiency of water, while soils which are poor in plant food will produce an abundant crop if the water be present in proper amounts and have proper and timely access to the rootlets of the plant. The study, therefore, of the water movement in the soil, whether laterally, upward, or downward, is of the utmost practical importance. The methods of a study of this kind have been well established by King.[2]

The plant food of the soil, it is well understood, only has access to the absorbent organs of the plant when presented in a proper soluble or semi-soluble form in connection with water. From a chemical standpoint, in connection with the subject under discussion, the movement of water in the soil should be considered in connection, not alone with its power of dissolving plant foods, but with especial reference to its power of carrying them not only away from the reach of the roots of the plant, but even out of the field and into the streams and rivers and eventually into the sea. For our present purpose, therefore, we have only need to examine lysimetric observations for the

[1] "Some Physical Properties of Soils," U. S. Weather Bureau, Bulletin No. 4.
[2] Ninth Annual Report of the Wisconsin Experiment Station, p. 129, *et seq.*

purpose of determining the kinds of plant food which are most exposed to waste. It is not my purpose to take your time here with a vast array of figures, but I desire only to call your attention to the fact that of the chief plant foods, potash and the nitrates are the ones which are most exposed to loss.

The earliest systematic investigations of the quantity and composition of drainage were commenced at the Rothamsted Station by Lawes and Gilbert[1], in 1870. Lysimeters were constructed for the collection of the drainage water from thirty, forty, and sixty inches depth of soil, respectively, the soil and subsoil being kept in the natural state of aggregation.

Lawes and Gilbert call attention to the fact that, probably, at the Rothamsted Station, not more than five pounds of nitrogen are secured per acre each year from the atmosphere and the rain-water, while the average loss of nitrogen through the drainage water is over thirty pounds per acre. The quantity, of course, varies with the amount of rain-fall and the activity of nitrification. They speak of the possible exaggeration of the loss of nitrogen on account of the fact that the air had access to the soil both from below and above and therefore the process of nitrification where the lysimeters were placed might have been intensified.

Among the latest researches on this subject are those of Deherain.[2] It is pointed out by this author that the character of the crop grown upon the cultivated field has much to do with the determination of the loss of nitrogen per acre. Those crops which require an immense amount of moisture for their growth, such as the sugar beet, would tend thereby to prevent the loss of nitrogen in the drainage waters, the nitrates being stored in the beet instead of being given up to percolation. In general, it may be said that it is the quantity of the drainage water rather than its richness in nitrates which determines the total loss due to percolation, and from this it may be inferred that the loss by drainage is directly proportional to the rain-fall and inversely proportional to the magnitude of the harvest. The season at which the greatest loss takes place is also, there-

[1] *Jour. Roy. Agric. Soc.*, 17, 241-79 and 311-50; 16, 1-71.
[2] *Annales Agronomiques, February 25, 1893, pp. 65, et seq.*

fore, the one in which the growth of the plant is the least vigorous, provided that the vigor of nitrification and quantity of rain-fall remain the same. When plants grow vigorously and when they occupy the soil for a long time, the losses, due to drainage are reduced to a minimum. On the other hand, with plants which rapidly ripen, so that the harvest follows soon after the sowing, the losses are greater. The farmer, therefore, who suffers a failure of his crop, not only loses from the smallness of the harvest, but also by the percolation of the water through the soil. For this reason, it is obvious that leaving fields fallow is a very dangerous proceeding. Deherain found that fallow fields during the season lost as high as fifty kilograms of nitrogen per hectare, corresponding to 330 kilograms of nitrate of soda, worth seventy-six francs. These figures show plainly the magnitude of the losses which take place in the one item of nitrogen alone, due to the percolation of rain-water through the soil.

In this connection it may be of interest again to refer to the favorable action of lime in a great many soils in regard to its power of increasing the ability of a soil to hold the soluble plant foods against their removal by water. This favorable action is particularly manifested in many soils in the power of lime to increase their capacity for holding potash.

Warington explains this action of the lime salts, especially the carbonate, by suggesting that by combining with the acids of certain salts, as the carbonates, sulphates, chlorides, and nitrates, they allow the bases of these salts to unite with the hydrated metallic oxides. The carbonate of lime also converts the soluble acid phosphates, applied in manure, to the sparingly soluble calcium phosphates, which, as they gradually enter into solution are converted into ferric and aluminic phosphates. An admirable description of the absorptive power of soils has been given by Warington[1] and many other authors have also discussed this matter in detail.

We can see from the data given above how water continually acts upon a soil in the removal of certain soluble plant foods. It might be inferred from this that all arable soils exposed con-

[1] "Practice with Science," 2.

tinually to rains would soon be exhausted of all valuable, soluble plant food. But it has also been pointed out how certain constituents of the soil have a faculty of absorbing and retaining materials which are soluble in water under ordinary conditions. It must not be forgotten also that the rain-water which descends upon the earth is not pure. Rain-water brings to the earth a certain amount of valuable plant food. Not only does it absorb and hold in solution ammonia and nitric acid, which may be formed by the electrical discharges in the air, but it also collects and brings to the surface of the earth vast quantities of meteoric dust containing valuable fertilizing principles. Thus we have constantly entering the soil water which contains more or less of the materials necessary to plant growth. Even the drainage waters, which leave an arable field, may not reach the sea without giving up much of this material. The drainage waters in passing underneath the earth's surface take devious courses and are often brought near to the surface again or are poured upon soils which are quite different in their texture from those furnishing the materials in solution. Sterry Hunt[1] has pointed out how such waters sooner or later come upon permeable strata by which they are absorbed and in their subterranean circulation undergo important changes. Especially when these waters reach argillaceous strata their content of neutral, soluble salts may suffer great changes. Such waters charged with organic and mineral materials contain usually large amounts of potassium salts and notable quantities of silica and phosphates, and in many cases ammoniated salts, and nitrites or nitrates.

The experiments of Way, Voelcker, and others have shown that in contact with argillaceous sediments these waters give up their potash, ammonia, silica, phosphoric acid and organic matter, which remain in combination with the soil; on the other hand, soda, magnesia, sulphuric acid and chlorine are not removed from the drainage waters. Eichorn attributes this power of selective absorption in the soil chiefly to the action of hydrated double aluminum silicates, and supposes that the process is one of double exchange, equivalents of lime or soda being given up for the potash retained. By this power of

[1] "Chemical and Geological Essays," 95.

selective absorption the mineral matters required for the growth of plants tend to be retained in most soils, while those not required for the growth of plants are removed. Nevertheless, much of the valuable mineral material in solution must escape absorption and finally find its way into the streams, rivers, and seas.

From the foregoing summary of the methods of waste of plant food it has been seen that in spite of all the precautions of the farmer and the chemist, and in spite of the selective absorption of the soil, immense quantities of valuable plant food are carried into the sea, where apparently they are lost to agriculture forever. But this is only an apparent loss. The economies of nature are so happily adjusted as to provide a means of gradually returning in some form or other to the power of the farmer the plant food which has been apparently destroyed. It is true that this return will probably not be to the locality where the waste originally occurred, and it may not take place until after the lapse of thousands of years, but this is of no consequence. Provided arable lands in general receive in some way and at some time a certain return for the plant food removed, it is entirely immaterial whether this be the original plant food removed or other equally as good.

The sea is the great sorting ground into which all this waste material is poured. The roller processes of nature, like the mills of the gods, grind exceedingly slow and small, and the sea becomes the bolting cloth by which the products of milling are separated and sorted out. As soon as this waste material is poured into the sea, the process of sorting at once begins. The carbonate of lime becomes deposited in vast layers, or by organic life is transformed into immense coral formations or into shells. Phosphoric acid is likewise sifted out into phosphatic deposits or passes into the organic life of the sea. Even the potash, soluble as it is, becomes collected into mineral aggregates or passes into animal or vegetable growth. All these valuable materials are thus conserved and put into a shape in which they may be returned sooner or later, to the use of man. In the great cosmic economy there is no such thing as escape from usefulness of any valuable material.

Sterry Hunt[1] has called especial attention to this sifting and sorting power of water and the important part it plays in the formation of crystalline rocks. "Igneous fusion," he says, "destroys the mineral species of the crystalline and brings them back as nearly as possible to the great primary and undifferentiated material. This is the great destroyer and disorganizer of mineral as well as of organic matter. Subterranean heat in our time acting on buried aqueous sediments destroys carbonates, sulphates, and chlorides, with the evolution of acidic gases and the generation of basic silicates and thus repeats in miniature the conditions of the anteneptunian chaos.

"On the other hand each mass of cooling igneous rock in contact of water begins anew the formative process. The hydrated amorphous product palagonite, is, if we may be allowed the expression, a sort of silicated protoplasm and by its differentiation yields to the solvent action of water, the crystalline silicates which are the constituent elements of the crenitic rocks, leaving at the same time a more basic residuum abounding in magnesia and iron oxide and soluble not by crenitic but subaerial action."

Let me call attention, for a few moments, to some of the more important ways, pointed out through the researches of agricultural chemists, in which these waste products are restored. We are inclined to look upon the sea as devoid of vegetable growth, but the gardens of the sea are no less fully stocked with economic plants than the gardens of the land. The sea-weeds of all genera and species are constantly separating valuable materials from the waters of the ocean and placing them again in organic form. Many years ago Forchhammer[2] pointed out the agricultural value of certain fucoids. Many chemists have contributed important data in regard to the composition of these bodies. Jenkins[3] gives analyses of several varieties of sea-weed, showing that in the green state it is quite equal to stall manure. The farmers are said to pay as high as five cents a bushel for it. Goessmann[4] also gives analyses of several varieties of sea-weed.

[1] *Mineral Physiology and Physiography*, 188.
[2] *J. prakt. Chem.*, 1st. Series. 38, 388.
[3] Annual Report, Conn. State Exp't. Sta., *1890*, 72
[4] Annual Report, Mass. State Exp't. Sta., *1887*, 223.

We are indebted, however, to the reports of Wheeler and Hartwell[1] for the fullest and most systematic discussion of the agricultural value of sea-weeds which has been published. Their interesting and elaborate report was published in January, 1893. Those who are interested in the details of this work can find all known publications on the subject properly arranged, classified, and studied in the publication mentioned. We learn from this publication that sea-weed was used as a fertilizer as early as the fourth century, and its importance for this purpose has been recognized more and more in modern days, especially since chemical investigations have shown the great value of the food materials contained therein.

To show the commercial importance of sea-weed as a fertilizer, it is only necessary to call attention to the fact that in 1885 its value for use as fertilizer in the State of Rhode Island was $65,044, while the value of all other commercial fertilizers was only $164,133. While sea-weed, in a sense, can only be successfully applied to littoral agriculture, yet the extent of agricultural lands bordering on the sea is so great as to render the commercial importance of the matter of the highest degree of interest.

It is not my intention here to enter into the discussion of the methods of preparing the sea-weed, the times at which it should be gathered and the best means of applying it to the soil; these matters are all thoroughly discussed by Wheeler and Hartwell in the publication mentioned. As an instance of the value of sea-weed at a point far removed from the Rhode Island coast, I may be permitted to say that near the mouth of the Caloosahatchee river, at the town of Ft. Meyers. I saw the most happy effects produced in intensive culture by the application of sea-weed alone to the sandy soils bordering on this arm of the sea. Dr. Washburn, of the Florida Experiment Station, was conducting the experiments to which I refer and he spoke in the highest terms of the value of the sea-weed in his work. Thousands of tons of this sea-weed are allowed to go to waste annually along these shores, simply because the agriculturist has not been informed in regard to its fertilizing value.

There are many other uses for sea-weed besides the agricul-

[1] Rhode Island Exp't. Sta. Bull. 21.

tural one but in these we are not much interested, except incidentally. Many of the varieties of sea-grass are used for filling mattresses, cushions, etc. Other varieties are burned and their ashes used for the manufacture of soda, iodine, and bromine. The gelatinous portions of sea-weeds become exceedingly hard and elastic upon being dried and have been molded into various forms as substitutes for horn and shells in making handles for knives, files, and other tools. In the Techno-Chemical receipt book, on page 177, may be found receipts for making artificial ebony from the charcoal obtained from sea-weeds; also for making leather, soap, and glue. For the latter purpose the plants are dried and powdered, extracted with warm water, with or without the addition of alcohol. The solution is allowed to settle at a temperature of 120° F. When cool it forms a jelly which is used for various purposes. The direction is then given for making transparent sea-weed leather, opaque sea-weed leather, sea-weed soap, and sea-weed glue.

No attempt can be made to give the quantities of sea-weed which are annually cast upon the shores of the different continents. Perhaps Rhode Island is no more favored in this respect than any other locality and we have seen the value of the sea-weed which was gathered for agricultural purposes in that State alone. The amount gathered represents only a very small fraction of the amount which was thrown upon the shores. It is easy, therefore, to conclude that the quantities of nitrogen, phosphoric acids and potash annually removed from the seas by the plants living therein are no less great in magnitude than those removed from the land by crops and plants of all kinds.

But sea-weed and other vegetable products of the sea are not the only vehicles in which the plant food in solution in the waters of the ocean may be returned to the uses of man. The animal life of the ocean is not less important than that of the land. In the animal economy of the ocean are gathered, therefore immense quantities of valuable food material which are thus placed in a condition to be at least in part restored in the form of food. Relatively, phosphoric acid and nitrogen are restored in much greater quantities than potash. The composition of fish in general shows that relatively larger quantities of

phosphoric acid and nitrogen are found than of fat and potash. The chemical composition of the nutritive portion of fishes has been thoroughly investigated by Atwater.[1]

The percentage of phosphoric acid in the flesh of American fishes, in its fresh state, is about one-half of one per cent. In one instance, that of smelt, Atwater found, 0.81 per cent. in the flesh of the fish. In the water-free substance of the flesh the percentage of phosphoric acid in round numbers is 2.5. In the case of the smelt above mentioned it amounted to 5.49 per cent. When it is considered that the bones and other refuse of the fish presumably richer in phosphoric acid than the flesh, were not included in this investigation, the quantity of phosphoric acid in fish is distinctly brought to view.

The quantity of albuminoids in the water-free substance of the flesh of fish is enormously high as compared with that of ordinary foods. In round numbers it may be said to be about 75 per cent. of the total water-free substance. In some cases the albuminous matter, or in other words the protein, makes up almost the whole of the water-free substance as in the case of a brook trout, quoted by Atwater, in which the percentage of protein in the dry flesh was 93.25; and of a perch in which it was 93.33; and of a sea bass in which it was 95.88; and a red snapper in which it was 95.38, and others in which even a higher percentage was reported.

It is thus seen that the ordinary fishes of the ocean collect, especially the two great elements of plant food, phosphorus, and nitrogen.

Oysters and other shell fishes collect not only large quantities of phosphorus and nitrogen, but also larger quantities of carbonate of lime. As has been intimated in another place, it is entirely probable that in earlier times when the sea was richer in phosphoric acid than at present, considerable quantities of phosphate of lime may have been secreted with the carbonate of lime in the shell. At the present time, however, the phosphate of lime has almost or quite disappeared from the matters of which shells are composed.

[1] The Chemical Composition and Nutritive Values of Food Fish and Aquatic Vertebrates, by W. O. Atwater. Report of the U. S. Commissioner of Fish and Fisheries, *1883*, 679-868.

While the art of fishing is practiced chiefly for the purpose of gaining human food, yet in many large fishing districts the fish waste becomes valuable fertilizing material. Some kinds of fish, as the menhaden, are, however, collected chiefly for their fertilizing value. The use of fish for fertilizing purposes is not new. A most interesting description of the use of agricultural fertilizers by the American Indians is given by Goode.[1] As long ago as 1875 the value of the nitrogen derived from the menhaden was estimated to be about two million dollars. In the year 1878 it is estimated that 200,000 tons of menhaden fish were captured between Cape Henry and the Bay of Fundy. The oil is first extracted from the fish for commercial purposes and afterward the residue is dried and ground and sold to farmers and fertilizer manufacturers. For a complete history of the menhaden the articles of Prof. G. Brown Goode, in the report of the U. S. Commissioner of Fish and Fisheries for 1877 and 1879, may be consulted.

The honor of teaching the American colonists the use of artificial fertilizers belongs, without doubt, to an Indian named Squanto. In Governor Bradford's "History of Plimouth Plantation" is given an account of the early agricultural experiences of the Plymouth colonists. In April, 1621, at the close of the first long dreary winter "they (as many as were able) began to plant their corne, in which service Squanto (an Indian) stood them in great stead, showing them both ye manner how to set it, and after how to dress and tend it. Also he tould them, axcepte they got fish and set with it (in these old grounds) it would come to nothing; and he showed them yt in ye middle of Aprili, they should have store enough come up ye brooke by which they begane to build and taught them how to take it."[2]

Another account mentioned by Goode of the practice of the Indians in this respect may be found in George Mourt's "Relation or Journal of the Beginning and Proceedings of the English Plantation settled at Plimouth in New England, by certain English Adventurers, both merchants and others, London, 1622." "We set the last spring some twenty acres of Indian corn, and

[1] American Naturalist, 14, July, *1880*, No. 7., 473, *et seq.*
[2] Coll. Mass. Hist. Soc., 4th Series, 3, 100, *1856*.

sowed some six acres of barley and pease, and, according to the manner of the Indians, we manured our ground with herrings, or rather shads, which we have in great abundance and take with great ease at our doors. Our corn did prove well, and God be praised, we had a good increase of Indian corn, and our barley indifferent good."[1]

Thomas Morton, in his "New England Canaan," London, 1632, wrote of Virginia: "There is a fish (by some called shadds, by some, allizes,) that at the spring of the yeare passe up the rivers to spawn in the pond, and are taken in such multitudes in every river that hath a pond at the end that the inhabitants doung their ground with them. You may see in one township a hundred acres together, set with these fish, every acre taking 1,000 of them, and an acre thus dressed will produce and yield so much corn as three acres without fish; and (least any Virginea man would infere hereupon that the ground of New England was barren, because they use more fish in setting their corne, I desire them to be remembered, the cause is plaine in Virginea) they have it not to sett. But this practice is onely for the Indian maize (which must be set by hands), not for English grain; and this is, therefore, a commodity there."

The following amusing study quoted by Goode is taken from the records of the town of Ipswich, May 11, 1644:

"It is ordered that all the doggs for the space of three weeks from the publishing hereof, shall have one legg tyed up, and if such a dog shall break loose and be found doing harm the owner of the dogg shall pay damage. If a man refuse to tye up his dogg's legg and hee bee found scraping up fish in a cornfield, the owner thereof shall pay twelve pence damage beside whatever damage the dogg doth. But if any fish their house lotts and receive damage by doggs, the owners of these house lotts shall bear the damage themselves."

The practice of using fish, therefore, for fertilizing purposes, is many centuries old, but until recent years the farmers residing along the coast were the only ones who received any benefit therefrom; but since the more careful scientific study of the value of fish fertilization, the nitrogenous elements taken from

[1]Coll. Mass. Hist. Soc., 2nd Series, 9, *1832*, 60.

505.A56

the sea by the fish now find their way not only to the gardens and truck farms along the New England and New Jersey coasts, but also to the wheat fields of Ohio and the cotton fields of North Carolina.

Conservation of Nitrogen.—Attention has been called to the manner in which the nitrogen carried into the ocean by the waste of the land is returned in great part through the marine, vegetable, and animal life. Immense quantities of waste nitrogen, however, are further secured, both from sea and land, by the various genera of birds. The well-known habits of birds in congregating in rookeries during the nights, and at certain seasons of the year tends to bring into a common receptacle the nitrogenous matters which they have gathered and which are deposited in their excrement and in the decay of their bodies. The feathers of birds are particularly rich in nitrogen, and the nitrogenous content of the flesh of fowls is also high. The decay, therefore, of remains of birds, especially if it take place largely excluded from the leaching of water, tends to accumulate vast deposits of nitrogenous matter. If the conditions in such deposits are favorable to the processes of nitrification, the whole of the nitrogen, or at least the larger part of it, which has been collected in this débris, becomes finally converted into nitric acid and is found combined with appropriate bases as deposits of nitrates. The nitrates of the guano deposits and of the deposits in caves arise in this way. If these deposits are subject to moderate leaching the nitrate may become infiltered into the surrounding soil, making it very rich in this form of nitrogen. The beds and surrounding soils of caves are often found highly impregnated with nitrates.

While for our purpose, deposits of nitrates only are to be considered which are of sufficient value to bear transportation, yet much interest attaches to the formation of nitrates in the soil even when they are not of commercial importance.

In many soils of tropical regions not subject to heavy rainfalls, the accumulation of these nitrates is very great. Müntz and Marcano[1] have investigated many of these soils to which attention was called first by Humboldt and Boussingault.

[1] *Compt. rend.*, 101, *1885*, 65, *et seq.*

They state that these soils are incomparably more rich in nitrates than the most fertile soils of Europe. The samples which they examined were collected from different parts of Venezuela and from the valleys of the Orinoco as well as on the shore of the Sea of Antilles. The nitrated soils are very abundant in this region of South America where they cover large surfaces. Their composition is variable, but in all of them carbonate and phosphate of lime are met with and organic nitrogenous material. The nitric acid is found always combined with lime. In some of the soils as high as thirty per cent. of nitrate of lime have been found. Nitrification of organic material takes place very rapidly the year round in this tropical region. These nitrated soils are everywhere abundant around caves, as described by Humboldt, caves which serve as the refuge of birds and bats. The nitrogenous matters, which come from the decay of the remains of these animals, form true deposits of guano which are gradually spread around, and which in contact with the limestone and with access of air, suffer complete nitrification with the fixation of the nitric acid by the lime.

Large quantities of this guano are also due to the débris of insects, fragments of elytra, scales of the wings of butterflies, etc., which are brought together in those places by the millions of cubic meters. The nitrification, which takes place in these deposits, has been found to extend its products to a distance of several kilometers through the soil. In some places the quantity of the nitrate of lime is so great in the soils that they are converted into a plastic paste by this deliquescent salt.

It is suggested by the authors that the co-existence of the nitrate and phosphate of lime is sufficient in all cases to demonstrate the organic origin of the nitric acid. It would not be possible to attribute such an origin to the nitrate present in these soils if it could not be determined that it was thus associated with phosphate and other remains, the last witnesses of a former animal life.

As a result of the observations of Müntz and Marcano, they conclude that it is not proper to accredit to the electrical discharges in the atmosphere the origin of the nitric acid forming

these deposits although they admit primarily the source of the nitric acid may have been due to electricity, but that it first was passed through the organism of the plant and thence into that of the animal whence it is accumulated in the deposits referred to.

The theory of Müntz and Marcano in regard to the nitrates of soils, especially in the neighborhood of caves, is probably a correct one, but there are many objections to accepting it to explain the great deposits of nitrate of soda which occur in many parts of Chile. Another point, which must be considered also, is this: That the processes of nitrification can not now be considered as going on with the same vigor as formerly. Some moisture is necessary to nitrification, as the nitrifying ferment does not act in perfectly dry soil, and in many localities in Chile where the nitrates are found it is too dry to suppose that any active nitrification could now take place.

The existence of these nitrate deposits has long been known.[1] The old Indian laws originally prohibited the collection of the salt, but nevertheless it was secretly collected and sold. Up to the year 1821, soda saltpeter was not known in Europe except as a laboratory product. About this time the naturalist, Mariano de Rivero, found on the Pacific coast, in the Province of Tarapacá, immense new deposits of the salt. Later the salt was found in equal abundance in the Territory of Antofogasta and further to the south in the desert of Atacama, which forms the Department of Taltal.

At the present time the collection and export of saltpeter from Chile is a business of great importance. The largest export which has ever taken place in one year was in 1890, when the amount exported was 927,290,430 kilograms; of this quantity 642,506,985 kilograms were sent to England and 86,124,870 kilograms to the United States. Since that time the imports of this salt into the United States have largely increased.

According to Pissis[2] these deposits are of very ancient origin. This geologist is of the opinion that the nitrate deposits are the result of the decomposition of feldspathic rocks; the bases thus

[1] A most interesting article on the subject may be found in *Jour. Roy. Agric. Soc.*, *1852*, 13, 349, *et seq.*

[2] Fuchs and De Launy, *Traité des Gîtes Mineraux*, *1893*, 1, 425.

produced gradually becoming united with the nitric acid provided from the air.

According to the theory of Nöllner[1] the deposits are of more modern origin and due to the decomposition of marine vegetation. Continuous solution of soils beneath the sea gives rise to the formation of great lakes of saturated water, in which occurs the development of much marine vegetation. On the evaporation of this water, due to geologic isolation, the decomposition of nitrogenous organic matter causes generation of nitric acid, which, coming in contact with the calcareous rocks, attacks them, forming nitrate of calcium, which, in presence of sulphate of sodium, gives rise to a double decomposition into nitrate of soda and sulphate of calcium.

The fact that iodine is found in greater or less quantity in Chile saltpeter is one of the chief supports of this hypothesis of marine origin, inasmuch as iodine is always found in sea plants and not in terrestrial plants. Further than this, it must be taken into consideration that these deposits of nitrate of soda contain neither shells nor fossils, nor do they contain any phosphate of lime. The theory, therefore, that they were due to animal origin is scarcely tenable.

Lately extensive nitrate deposits have been discovered in the U. S. of Columbia.[2] These deposits have been found extending over thirty square miles and vary in thickness from one to ten feet. The visible supply is estimated at 7,372,800,000 tons, containing from 1.0 to 13.5 per cent. of nitrate. The deposits consist of a mixture of nitrate of soda, chloride of soda and sulphate of calcium, sulphate of alumina, and insoluble silica. It is thought that the amount of these deposits will almost equal those in Chile and Peru.

Phosphatic Deposits.—Gautier[3] calls attention to the fact that the oldest phosphates are met with in the igneous rocks, such as basalt, trachyte, etc., and even in granite and gneiss. It is from these inorganic sources, therefore, that all phosphatic plant food must have been drawn. In the second order in age

[1] El Salitre de Chile, René F Le Feuvre y Arturo Dagino, *1893*, 12.

[2] Bureau of American Republics, *Monthly Bulletin*, December, *1893*, 18, *et seq.*

[3] *Compt. rend.*, **116**, 1271, 6.

Gautier places the phosphates of hydro-mineral origin. This class not only embraces the crystalline apatites, but also those phosphates of later formation, formed from hot mineral waters in the jurassic, cretaceous, and tertiary deposits.

These deposits are not directly suited to nourish plants.

The third group of phosphates in order of age and assimilability embraces the true phosphorites containing generally some organic matter. They are all of organic origin. In caves where animal remains are deposited there is an accumulation of nitrates and phosphates.

Not only do the bones of animals furnish phosphates, but they are also formed in considerable quantities by the decomposition of substituted glycerides such as lecithin.

The ammonia produced by the nitrification of the albuminoid bodies combines with the free phosphoric acid thus produced, forming ammonium or diammonium phosphates.

The presence of ammonium phosphates in guanos was first noticed by Chevreul more than half a century ago.

If such deposits overlay a pervious stratum of calcium carbonate, such as chalk, and are subject to leaching, a double decomposition takes place as the lye percolates through the chalk. Acid calcium phosphate and ammonium carbonate are produced. By further nitrification the latter becomes finally converted into calcium nitrate. In like manner aluminum phosphates are formed by the action of decomposing organic matter on clay.

Davidson[1] explains the origin of the Florida phosphates by suggesting that they arose chiefly through the influx of animals driven southward by the glacial period. According to his supposition the waters of the ocean, during the cenozoic period contained more phosphorus than at the present time. The waters of the ocean over Florida were shallow and the shell fish existing therein may have secreted phosphate as well as carbonate of lime. This supposition is supported by an analysis of a shell of *lingula ovalis*, quoted by Dana, in which there were 85.79 per cent. of lime phosphate. In these waters were also many fishes of all kinds and their débris served to increase the

[1] *Engineering and Mining Journal*, quoted in the "Phosphates of America," by Wyatt 66, *et seq.*

amount of this substance. As the land emerged from the sea came the great glacial epoch driving all terrestrial animals southward. There was therefore a great mammal horde in the swamps and estuaries of Florida. The bones of these animals contributed largely to the phosphatic deposits. In addition to this, the shallow sea contained innumerable sharks, manatees, whales and other inhabitants of tropical waters, and the remains of these animals added to the phosphatic store.

While these changes were taking place in the quaternary period, the Florida peninsula was gradually rising and as soon as it reached a considerable height, the process of denudation by the action of water commenced. Then there was a subsidence and the peninsula again passed under the sea and was covered with successive layers of sand. The limestones during this process, had been leached by rain-water containing an excess of carbonic acid. In this way the limestones were gradually dissolved while the insoluble phosphate of lime was left in suspension. During this time the bones of the animals before mentioned by their decomposition added to the phosphate of lime present in the underlying strata, while some were transformed into fossils of phosphate of lime just as they are found to-day in vast quantities.

Wyatt[1] explains the phosphate deposits somewhat differently. According to him, during the miocene submergence there was deposited upon the upper eocene limestones, more especially in the cracks and fissures resulting from their drying up, a soft, finely disintegrated calcareous sediment or mud. The estuaries formed during this period were swarming with animal and vegetable life, and from this organic life the phosphates were formed by decomposition and metamorphism due to the gases and acids with which the waters were charged.

After the disappearance of the miocene sea there were great disturbances of the strata. Then followed the pliocene and tertiary periods and quaternary seas with their deposits and drifts of shells, sands, clays, marls, bowlders and other transported materials, supervening in an era when there were great fluctuations of cold and heat.

[1] *Engineering and Mining Journal*, August 23, *1890*.

By reason of these disturbances the masses of the phosphate deposits which had been infiltrated in the limestones became broken up and mingled with the other débris and were thus deposited in various mounds or depressions. The general result of the forces which have been briefly outlined, was the formation of bowlders, phosphatic débris, etc. Wyatt therefore classifies the deposits as follows:

1. Original pockets or cavities in the limestone filled with hard and soft rock phosphates and débris.

2. Mounds or beaches, rolled up on the elevated points, and chiefly consisting of huge bowlders of phosphate rock.

3. Drift or disintegrated rock, covering immense areas, chiefly in Polk and Hillsboro counties, and underlying Peace river and its tributaries.

N. H. Darton, of the U. S. Geological Survey, ascribes the phosphate beds of Florida to the transformation of guano.[1] According to this author two processes of decomposition have taken place; one of these is the more or less complete replacement of the carbonate by the phosphate of lime; the other is a general stalactitic coating of phosphatic material. Darton further calls attention to the relation of the distribution of the phosphate deposits as affecting the theory of their origin, but does not find any peculiar significance in the restriction of these deposits to the western ridge of the Florida peninsula.

As this region evidently constituted a long, narrow peninsula during early miocene times it is a reasonable, tentative hypothesis that during this period guanos were deposited from which was derived the material for the phosphatization of the limestone either at the same time or soon after.

Darton closes his paper by saying that the phosphate deposits in Florida will require careful, detailed geologic exploration before their relations and history will be fully understood.

According to Dr. N. A. Pratt the rock or bowlder phosphate had its immediate origin in animal life and the phosphate bowlder is a true fossil. He supposes the existence of some species in former times in which the shell excreted was chiefly phosphate of lime. The fossil bowlder, therefore,

[1] *Amer. Jour. of Science*, 41, February, *1891*.

becomes the remains of a huge foraminifer which had identical composition in its skeleton with true bone deposits or of organic matter.

Perhaps the most complete exposition of the theory of the recovery of waste phosphates, with especial reference to their deposition in Florida, has been given by Eldridge,[1] of the U. S. Geological Survey. Eldridge calls attention to the universal presence of phosphates in sea water and to the probability that in earlier times, as during the miocene and eocene geologic periods, the waters of the ocean contained a great deal more phosphate in solution than at the present time. He cites the observations of Bischof, which show the solubility of different phosphates in waters saturated with carbon dioxide. According to these observations apatite is the most insoluble form of lime phosphate, while artificial basic slag phosphate is the most soluble. Among the very soluble phosphates, however, are the bones of animals, both fresh and old. Burnt bones, however, are more soluble than bones still containing organic matter. Not only are the organic phosphates extremely soluble in water saturated with carbon dioxide but also in water which contains common salt or chloride of ammonium. The presence of large qauntities of common salt in sea water would, therefore, tend to increase its power of absorbing lime phosphates of organic origin. It is not at all incredible, therefore, to suppose that at some remote period the waters of the ocean, as indicated by these theories, were much more highly charged with phosphates than at the present time.

According to Eldridge, the formation of the hard rock and soft phosphates may be ascribed to three periods: First, that in which the primary rock was formed; second, that of secondary deposition in the cavities of the primary rock; third, that in which the deposits thus formed were broken up and the resulting fragments and comminuted material were redeposited as they now occur.

"The first of these stages began probably not later than the close of the older miocene, and within the eocene area it may

[1] A preliminary sketch of the phosphates of Florida. By Geo. H. Eldridge, author's edition, *1892*, 18, *et seq.*

have begun much earlier. Whether the primary phosphate resulted from a superficial and heavy deposit of soluble guanos, covering the limestones, or from the concentration of phosphate of lime already widely and uniformly distributed throughout the mass of the original rock, or from both, is a difficult question. In any event, the evidence indicates the effect of the percolation of surface-waters, highly charged with carbonic and earth-acids, and thus enabled to carry down into the mass of the limestone dissolved phosphate of lime, to be redeposited under conditions favorable to its separation. Such conditions might have been brought about by the simple interchange of bases between the phosphate and carbonate of lime thus brought together, or by the lowering of the solvent power of the waters through loss of carbonic acid. The latter would happen whenever the acid was required for the solution of additional carbonate of lime, or when, through aeration, it should escape from the water. The zone of phosphate-deposition was evidently one of double concentration, resulting from the removal of the soluble carbonate thus raising the percentage of the less soluble phosphate, and from the acquirement of additional phosphate of lime from the overlying portions of the deposit."

"The thickness of the zone of phosphatization in the eocene area is unknown, but it is doubtful if it was over twenty feet. In the miocene area the depth has been proved from the phosphates *in situ* to have been between six and twelve feet."

The deposits of the secondary origin, according to Eldridge, are due chiefly to sedimentation, although some of them may have been due to precipitation from water. This secondary deposition was kept up for a long period, until stopped by some climatic or geologic change. The deposits of phosphates thus formed in the Florida peninsula are remarkably free from iron and aluminum, in comparison with many of the phosphates of the West Indies.

The third period in the genesis of the hard-rock deposits embraces the period of formation of the original deposits and their transportation and storage as they are found at the present time. The geologic time at which this occurred is somewhat uncertain but it was probably during the last submergence of the peninsula.

In all cases the peculiar formation of the Florida limestone must be considered. This limestone is extremely porous and, therefore, easily penetrated by the waters of percolation. A good illustration of this is seen on the southwestern and southern edges of Lake Okeechobee. In following down a drainage canal which had been cut into the southwest shore of the lake I saw the edge of the basin, which is composed of this porous material. The appearance of the limestone would indicate that large portions of it had already given way to the process of solution. The remaining portions were extremely friable, easily crushed, and much of it could be removed by the ordinary dredging machines. Such a limestone as this is peculiarly suited to the accumulation of phosphatic materials, due to the percolation of the water containing them. The solution of the limestone and consequent deposit of the phosphate of lime is easily understood when the character of this limestone is considered.

Shaler, as quoted by Eldridge in the work already referred to, refers to this characteristic of the limestone and says that the best conditions for the accumulation of valuable deposits of lime phosphate in residual débris appear to occur where the phosphatic lime marls are of a rather soft character; the separate beds having no such solidity as will resist the percolation of water through innumerable incipient joints such as commonly pervade stratified materials, even when they are of a very soft nature.

Eldridge is also of the opinion that the remains of birds are not sufficient to account for the whole of the phosphatic deposits in Florida. He ascribes them to the joint action of the remains of birds, of land and marine animals and to the deposition of the phosphatic materials in the waters in the successive subsidence of the surface below the water line.[1]

Potash Deposits.—In the foregoing pages I have tried to set clearly before you the different ways in which the waste of nitrogen and phosphoric acid has been recovered by nature in a form suitable for restoration to arable fields. In the case of potash, however, we have seen that this

[1] For an elaborate discussion of phosphate deposits consult *Gîtes Mineraux, par Fuchs et DeLauny*, 309, *et seq.*

element is not restored by the processes already mentioned, in amounts proportionate to nitrogen and phosphorus. Potash salts, being extremely soluble, are likely to be held longest in solution. Some of them, of course, are recovered in the animal and vegetable life, of which we have spoken, but the great mass of potash carried into the sea still remains unaccounted for. The recovery of the waste of potash is chiefly secured by the isolation of sea waters containing large quantities of this salt and their subsequent evaporation. Such isolation of sea waters takes place by means of geologic changes in the level of the land and sea. In the raising of an area above the sea level there is almost certain to be an enclosure, of greater or less extent, of the sea water in the form of a lake. This enclosure may be complete or only partial, the enclosed water area being still in communication with the main body of the sea by means of small estuaries. If this body of water be exposed to rapid evaporation, as was doubtless the case in past geologic ages, there will be a continual influx of additional sea water through these estuaries to take the place of that evaporated. The waters may thus become more and more charged with saline constituents. Finally a point is reached in the evaporation when the less soluble of the saline constituents begin to be deposited. In this way the various formations of mineral matter, produced by the drying up of inclosed waters, take place.

The most extensive deposits of potash known are those in the neighborhood of Stassfurt, in Germany. The following description probably represents the method of formation of these deposits:[1]

"The Stassfurt salt and potash deposits had their origin thousands of years ago, in a sea or ocean, the waters of which gradually receded, leaving near the coast, lakes which still retained communication with the great ocean by means of small channels. In that part of Europe the climate was still tropical, and the waters of these lakes rapidly evaporated but were constantly replenished through these small channels connecting them with the main body. Decade after decade this continued, until by evaporation and crystallization, the various salts pres-

[1] Potash, Columbian Exposition, German Kali Works 3-4.

ent in the sea water were deposited in solid form. The less soluble material, such as sulphate of lime or 'anhydrite,' solidified first and formed the lowest stratum. Then came common rock salt with a slowly thickening layer which ultimately reached 3000 feet, and is estimated to have been 13,000 years in formation. This rock salt deposit is interspersed with lamellar deposits of 'anhydrite,' which gradually diminish towards the top and are finally replaced by the mineral 'polyhalite,' which is composed of sulphate of lime, sulphate of potash, and sulphate of magnesia. The situation in which this polyhalite predominates is called the 'polyhalite region' and after it comes the 'kieserite region,' in which, between the rock salt strata, kieserite (sulphate of magnesia) is imbedded. Above the kieserite lies the 'potash region,' consisting mainly of deposits of carnallite, a mineral compound of muriate of potash and chloride of magnesia. The carnallite deposit is from 50 to 130 feet thick and yields the most important of the crude potash salts and that from which are manufactured most of the concentrated articles, including muriate of potash."

"Overlying this region is a layer of impervious clay which acts as a water-tight roof to protect and preserve the very soluble potash and magnesia salts, which, had it not been for the very protection of this overlying stratum, would have been long ages ago washed away and lost by the action of the water percolating from above. Above this clay roof is a stratum, of varying thickness of anhydrite, (sulphate of lime,) and still above this a second salt deposit, probably formed under more recent climatic and atmospheric influences or possibly by chemical changes in dissolving and subsequent precipitation. This salt deposit contains ninety-eight per cent. (often more) of pure salt, a degree of purity rarely elsewhere found. Finally, above this are strata of gypsum, tenacious clay, sand and limestone, which crop out at the surface."

"The perpendicular distance from the lowest to the upper surface of the Stassfurt salt deposits is about 5000 feet (a little less than a mile), while the horizontal extent of the bed is from the Harz Mountains to the Elbe River in one direction, and from the city of Madgeburg to the town of Bernburg in the other."

According to Fuchs and DeLauny[1] the saline formation near Stassfurt is situated at the bottom of a vast triassic deposit surrounding the city of Madgeburg. The quantity of sea water which evaporated to produce saline deposits of more than 500 meters in thickness must have been enormous and the rate of evaporation great. It appears that a temperature of 100° would have been quite necessary, acting for a long time, to produce this result.

These authors therefore admit that all the theories so far advanced to explain the magnitude of these deposits are attended with certain difficulties. What, for instance, could have caused a temperature of 100°? The most reasonable source of this high temperature must be sought for in the violent chemical action produced by the double decompositions of such vast quantities of salts of different kinds. There may also have been at the bottom of this basin some subterranean heat such as is found in certain localities where boric acid is deposited.

Whatever be the explanation of the source of the heat it will be admitted that at the end of the permian period there was thrown up to the northeast of the present saline deposits a ridge extending from Helgoland to Westphalia. This dam established throughout the whole of North Germany saline lagoons in which evaporation was at once established, and these lagoons were constantly fed from the sea.

There was then deposited by evaporation, first of all a layer of gypsum and afterwards rock salt, covering with a few exceptions the whole of the area of North Germany.

But around Stassfurt there occurred at this time geologic displacements, the saline basin was permanently closed and then by continued evaporation the more deliquescent salts, such as polyhalite, kieserite, and carnallite, were deposited.

These theories account with sufficient ease for the deposition of the saline masses, but do not explain why in those days the sea water was so rich in potash and why potash is not found in other localities where vast quantities of gypsum and common salt have been deposited. It may be that the rocks composing the shores of these lagoons were exceptionally rich in potash

[1] *Gites Mineraux*, 429.

and that this salt was, therefore, in a certain degree, a local contribution to the products of concentration.

Through the ages of the past, the rich stores of plant food have been steadily removed from arable fields and apparently forever lost. But in point of fact no particle of it has been destroyed. Even the denitrifying ferments described by Springer, Gayon and Dupetit, and Muntz, reduced only to a lower stage of oxidation or restore to a gaseous form the nitric nitrogen on which alone vegetables can feed. But electricity, combustion, and the activity of certain anaerobic ferments herding in the rootlets of legumes and other orders of plants, are able to recover and again make available this loss.

Lately Winogradsky and Warington have shown that an organism can be grown in a sugar solution containing certain salts, and excluding all nitrogenous matter save the free nitrogen of the atmosphere, which is capable of oxidizing and assimilating this inert gas. In a solution containing 7 grams of sugar as high as 14 milligrams of nitrogen have been fixed.

Warington says in speaking of this phenomenon:

"That a vegetable organism should be able to acquire from the air the whole of the nitrogen which it needs, is certainly very remarkable and is an extraordinary fact both to the physiologist and the chemist."[1]

The fact that a few million years may supervene before the particle that is carried off to-day as waste may return to organic life, shows the patience rather than the wastefulness of nature.

As a result of this general review of the migrations of plant food, the reassuring conclusion is reached that there is no danger whatever of the ultimate consumption or waste of the materials on which plants live. Circumscribed localities, through carelessness or ignorance, where once luxuriant crops grew, may become sterile, but the great source of supply is not exhausted. In fact, as the rocks decay and nitrifying organisms increase, the total store of plant food at the disposal of vegetation may continue to grow. When we join with this the fact that the skill of man in growing crops is rapidly increasing, we

[1] *Chem. News*, Oct. 13, *1893*, 170.

find no danger ahead in respect of the quantity of human food which may be produced.

Only the novelist might be able, by the aid of an unfettered imagination, to say how many human beings the United States alone will be able to feed in comfort. With the aid of scientific agriculture, with the help of the agricultural chemist we may safely say that a thousand million people will not so crowd our means of subsistence as to make Malthus more than a pleasing theorist. As I pointed out in my vice-presidential address at Buffalo, the death of humanity is not to come from starvation but from freezing, and many a geologic epoch will come and go before this planet dies of cold.

A NEW FORM OF AIR-BATH.[1]

By Ewald Sauer, Ph.D.

IN a recent article on the prevalent forms of air-baths, H. Petersen shows[2] conclusively that the designs ordinarily in vogue, whether made from copper or from aluminum,[3] are far removed from the ideal of such an apparatus. The deficiencies are chiefly in the direction of variable temperature and insufficient ventilation for the purpose of rapidly removing the liberated steam. The use of jacketed air-baths, as Soxhlet's apparatus,[4] while providing for constant temperature, limits the range of temperature to the boiling points of the liquids employed, and is subject also to limitations in size.

In order to obviate these difficulties, I have designed an air-bath, which while resembling externally the ordinary forms, differs from them in a few essential points. The main feature is the introduction of two bottoms which are connected with each other by several open tubes. These two bottoms are also joined together in the front and in the rear, while on the sides the space is open. A funnel-shaped opening in the center of the lower bottom allows the flame of an ordinary burner to freely

[1] Read before the Cincinnati Section, Oct. 14, *1893*.

[2] *Ztschr. angew. Chem.*, *1892*, 36.

[3] *Ber. d. chem. Ges.*, *1892*, 3637-40.

[4] *Ztschr. angew. Chem.*, *1891*, 363-68.

play on the lower surface of the upper or true bottom of the bath.

By means of this disposition the flame and the heated air current pass between the two bottoms about the series of connecting tubes, and issue on both sides. As a result, not only is the upper bottom heated, but also the series of tubes, while through the latter a current of hot air possessing the temperature of the upper bottom enters the interior of the bath. This hot current does double duty. In the first place it maintains a constant temperature in the bath; in the second, it effects a rapid removal of the aqueous vapor, which would be liberated as usual by the simple external heating.

That this device enables the chemist to secure the two desiderata of a constant temperature throughout the interior of the bath, and quick evaporation, is evident from the following tables of experimental results:

TABLE I.

Force of Bunsen burner flame.	Temperature upper part of air-bath, degrees.	Temperature lower part of air-bath, degrees.
I	220	215
½	128	127.5
	104.5	104.5
¼	83.5	83

The differences noted above are largely due to the different lengths of the mercury column of the thermometer enclosed in the heated space.

TABLE II.

Charge.	Temperature when empty.	Lowest temperature observed.	Temperature at close of evaporation.	Duration, minutes.	Grams of water evaporated.	Remarks.
5 grams asbestos and 10 grams water in a glass dish	124.5°	111°	120°	15	10	Several experiments with uniform results showed that the location of the charge in the bath did not affect the time required.
	118.5°	111°	115°	40	10	
10 grams water in an aluminum dish	124°	111°	114°	14	10	Several experiments showed conclusively that as soon as the water was completely evaporated the temperature returned rapidly to that indicated at the beginning.
	103°	96°	102°	14	10	
5 grams milk and 5 grams pumice stone in an aluminum dish	100.5°	92°	95°	12	5	Slight darkening of the residue.
	85°	82°	85°	15	5	

The end of the operation is readily recognized by the fact that no moisture issues from the upper openings (indicated by an arrow in the diagrams), *i.e.*, a cold beaker held over the openings is not dimmed.

These new air-baths are manufactured from both copper and aluminum by Max Kaehler & Martini, 50 Wilhelmstrasse, Berlin.

THE CHEMICAL AND PHYSICAL INVESTIGATION OF SOILS.[1]

By E. W. Hilgard, California.

I DESIRE to place before this Congress, without going into analytical details which will be set forth in a special report to the Association of Official Chemists, the general results of my long-continued studies on direct soil examination by physical and chemical means that have led me to attach to such examinations a far greater practical importance than is now usually assigned to them by the consensus of opinion both in Europe and America.

I premise that I was led into these investigations more particularly as a consequence of my almost continuous residence in the newer, thinly-settled or unsettled portions of this country, where the question of the fitness of lands for general agriculture, and their special adaptations are burning questions, which are there constantly pressed upon the attention of whosoever occupies a public position in connection with agricultural colleges or experiment stations. My researches have, therefore, borne essentially on virgin soils, or at least such as had been cultivated only for a short time and had received not even incidental fertilization.

With material so different from that which in Europe and in the eastern United States, have led most agricultural chemists to consider direct soil examination, and especially chemical soil analysis, as of little practical value, it is not surprising that I should have been led to conclusions differing somewhat widely from those commonly received; so that, while still agreeing that in the case of soils long fertilized, chemical analysis can give but little information as to the immediate producing power, I am satisfied that it can in the case of virgin soils be made of the most direct and vital use to the farmer and intending settler.

The substitute recommended for direct soil examination, after the sweeping condemnation of soil analysis some fifty years ago, was and still is, to put the question to the soil by cultivation and fertilization with the simples, potash, phosphoric acid, and nitrogen; and to deduce therefrom the needs of the soil. It

[1] Read before the World's Congress of Chemists, August 24, 1893.

goes without saying that this is but unpalatable advice to give to a settler in new regions; while even to the farmer in the older countries the carrying-out of a cogent experiment is by no means so easy a task as the precept implies. Moreover, the latter leaves room for great uncertainty in respect to seasonal differences; and the physical peculiarities of the soil are therein left totally out of consideration, although these are just as frequently in fault as the chemical composition, and the farmer is by no means usually to be credited with the ability to determine these points.

In my view, therefore, the examination of soils for the benefit of the agricultural population is one of the most needful, and in the newer states most urgent tasks set before the experiment stations; provided, of course, that the results can be successfully applied to practice.

My attention has from the outset been strongly drawn to the accuracy and certainty with which experienced farmers will, in a region familiar to them, judge of the quality and adaptations of land by its natural vegetation; more particularly by the forest growth. It is obvious that if we could interpret correctly the physical and chemical qualities of soils that have determined the choice of certain plants that occupy them as a result of secular co-adaptation by the survival of the fittest, we should have as definite and much more cogent data than can be supplied us at best by the brief culture experiments we can make. This thought suggested itself to me in noting the invariable recurrence of certain plants on soils showing obvious physical and chemical peculiarities, such as "stiffness" or "lightness" on the one hand, and richness in lime or humus on the other. I therefore determined to test the idea by actual, systematic, examination of the soils in all their relations; and it is upon the results of this study, and of their *comparison with actual agricultural practice*, that my views in the premises are based. It need hardly be recalled to mind that, such relations once established, the conclusions flowing therefrom can be legitimately, and as experience shows, fruitfully, projected into cases in which the actual indications of natural vegetation are not available.

The first point requiring attention in such researches is, naturally, the observation of the soils in place, and the recording of all the peculiarities whether of occurrence, structure, derivation, depth, vegetation, local and general climate, and if possible, cultural experience. The taking of the sample to be examined must, of course, be made to conform to the particular conditions of each case, and not to arbitrarily prescribed precepts, above all things. All accidental, abnormal variations must be excluded by a proper selection of the localities, and by sampling the same soil in several places. That it is thus possible to obtain specimens correctly representing in all essentials a wide extent of country without excessive multiplication of samples, my experience has fully proved. The depth to which the "soil" sample should be taken is ordinarily the lower limit of coloration by humus; but should that depth exceed twelve inches, the presumable maximum depth of tillage, one sample should be taken to that depth only. The subsoil is what lies beneath that line of coloration; it is frequently advisable or necessary to sample the soil mass for each twelve inches down to six feet depth, since the nature of the subsoil is one of the most essential points to be observed in all cases.

The first operation I undertake upon any soil sample is to wash about ten grams of it in a beaker with a water current of definite velocity, while stirring actively with a rod. The residue of sand or gravel is examined, macroscopically and microscopically, for the determination of the chief constituent minerals and of their surface condition, whether sharp or much rounded. We thus gain at once a pretty definite estimate of its relations to its place of origin and of its parent rocks, and therefore of its probable general chemical character, it being presumable that the fine matter is of the same general nature as the coarse.

Then follows the "hand test" of the soil by crushing small lumps between the thumb and forefinger, dry at first; then, after wetting, observing the change of color on wetting, and then kneading, in order to test its contents of plastic clay.

The next step, logically, is the test of the relations of the soil to water or moisture. Since the perviousness to water coming from above is so variable according to the accidental condition

and the *modus operandi*, I prefer to determine, as more definite factors, the water capacity and the hygroscopic coefficient, both of which give very definite information in respect to the most essential physical properties of a soil.

In determining the *water capacity* it is quite essential to determine both the *maximum* and the *minimum*, and that in the lowest column of water with which one can operate; I place this at one cm. I use a cylindrical vessel with perforated bottom resembling the "test-lead sieve" of Plattner's blow-pipe chest, of twenty-five or fifty cc. capacity. This is filled with the fine earth, and after weighing placed in a shallow dish with a layer of water. Within about an hour it is saturated to the maximum capacity; it is then weighed, which gives the maximum. Then the wet soil is covered with soil, first air-dry, then with such as has been saturated with moisture, until its weight ceases to decrease by liquid absorption. The last weighing determines the minimum water capacity; the difference between the maximum and minimum indicates the greater or less height to which the soil will raise capillary, liquid water.

The hygroscopic coefficient, which contrary to prevailing doctrines I find to be of great importance to the welfare of plants in the arid regions, must be determined by exposing the soil to a fully saturated atmosphere for at least seven hours in a layer 1 mm. thick. Under such conditions, the amount absorbed remains practically the same within ordinary cellar temperatures, contrary to what (according to Knop's law) happens when the air is only partially saturated. We thus obtain a datum which bears a very definite ratio to the clay and humus contents of the soil and its drought-resisting qualities. But in order to obtain comparable results, the drying of the soil must be done at 200° C., for at 100° soils of high absorptive power will continue to lose moisture for weeks. The drying is therefore done in a paraffin bath. From the drying tube or bulb the quantities for the chemical determinations are weighed out.

In the question of the maximum size of grain to be admitted to the chemical analysis, I have also sought to determine by direct experiment the proper limit; instead of assuming an arbitrary one as is usually done, with the result that the chemists of each

country have adopted a different rule, and thus their work is rendered incapable of comparison. Thus the German stations have adopted a two mm. mesh for the fine earth sieve, while the French official rule is "one mesh to the millimeter," leaving the aperture an uncertain quantity because dependent upon the thickness of the wire used. As a matter of fact the aperture is about 0.75 mm. In this country one mm. clear aperture has been adopted by the majority of chemists. Thus it becomes impossible to compare with any degree of certainty the analyses of these different countries.

In 1872, having perfected my apparatus for mechanical soil analysis,[1] I caused an investigation of the question to be made by my assistant, Dr. R. H. Loughridge. The result (see *Am. J. Sci., January, 1874*) was to show that in the very generalized soil worked upon, seventy-five per cent. of the dissolved soil ingredients was contained in the colloidal clay remaining suspended in water after twenty-four hours, in a column 200 mm. high, and that solution by the hydrochloric acid employed practically ceased when the diameter of 0.025 mm. (0.5 mm. hydraulic value) was exceeded. It was thus apparent that the finest practicable mesh might safely be used for the "fine earth"; and this I found to be at 0.5 mm. aperture, equal to sixty-four mm. hydraulic value. That for direct comparison by percentages it would be better to come down a much smaller grain-size, is doubtless true; but this degree of fineness would involve elaborate preparations, and difficulties that would render such investigations few and far between. I have, therefore, used the 0.5 mm. mesh in all soil analyses made since under my direction; and as the sieves used in soil work of the surveys of Kentucky and Arkansas were very nearly of the same character, that work remains comparable with mine. But whatever may be the size chosen by any one, the quantitative determination of the grain-sizes of one mm. and two mm. diameter should be made a rule, in order that allowance may be made for them when comparisons are desired.

The preliminary tests made should determine, in a measure,

[1] I omit any detailed reference to this apparatus and the subject of mechanical soil analysis for the reason that the matter has of late had considerable discussion in journals and is prevented in full detail in a report to the Association of Official Chemists.

the quantities which it is desirable to use for analysis; since great inconvenience often arises from handling excessive amounts of the iron-alumina precipitate. With such balances and methods as we command at present, I do not think there exists any need of employing hundreds of grams in any ordinary cases. If in the case of ores the selling price is allowed to be governed by the assay of a few grams, it is difficult to see why in the case of a soil we should do otherwise, provided the sample has been well taken and prepared so as to be representative. If that has *not* been done, the taking of fifty grams instead of five will not help the matter much.

I usually weigh out from two and a-half to three grams for general analysis; from three to five for the (separate) determination of phosphoric acid by the molybdate method. When in a strongly clayey soil there is a great deal of calcium carbonate, so much alumina is usually dissolved as to render the handling even from the above amounts troublesome, and parting is best resorted to.

There has been a great deal of discussion in regard to the strength of the solvent to be used in soil analysis. All admit that carbonated water is too feeble to approximate to the assimilative power of plants; while "Aufschliessung" with hydrofluoric acid goes far beyond. It has appeared to me from the outset that we should, if possible, ascertain the possible maximum solvent effect that can be expected of *any* plant; and from the fact that calcium oxalate is of so frequent occurrence in roots, I have thought that oxalic acid might be regarded as the strongest solvent at their command. Now, as is well known; oxalic acid expels from the corresponding salts both hydrochloric and nitric acids. In general, therefore, it stands on a par with these; and it is from this standpoint that I originally determined to use, as the most convenient solvent, hydrochloric acid of medium strength. I have since had the question tested directly by substituting oxalic for hydrochloric acid in comparative analyses of one and the same soil; and while there were differences due to the difficulty soluble compounds formed by oxalic acid, yet the interpretation of the two analyses would, for practical purposes, have been precisely the same.

A series of experiments made by Loughridge in 1873 on one and the same soil with hydrochloric acid of different degrees of concentration showed that the maximum solvent effect was exerted, not by the strongest acid, but by that of about 1.115 sp. gr. I therefore adopted this as the standard acid for soil analysis. Another series of experiments showed that the action was made practically complete by a digestion on the steam bath for five days; this also was, therefore, adopted as the regulation time for the acid digestion, which is always done in a porcelain beaker covered with a watch glass, only half immersed in the steam so as to permit condensation of the acid volatilized. My practice has been to take ten times as many cc. of acid as grams of soil weighed out.

The analysis is then carried out essentially like that of any silicate, including the determination of the silica soluble in sodium carbonate solution, which is a very important datum in estimating the degree of decomposition and zeolite formation that has occurred in the soil. In most cases the silica so determined permits of being assigned to the alumina dissolved, as kaolinite; but to this there are numerous exceptions, there being often twice as much alumina as can be assigned to the silica set free by the acid. The only possible form in which this excess of easily soluble alumina can be present is that of *aluminum hydroxide*; which must, therefore, be considered as one of the normal constituents, notably in the case of highly calcareous, and especially of "alkali" soils.

The phosphoric acid is determined by the molybdate method in a separate and larger portion of material, which is previously ignited in order to determine the "loss by ignition." This latter item, while serving to make the result of the analysis sum up to 100 or thereabouts, is really of no practical significance; since it is made up, besides the combustible matter, of water of hydration from the kaolinite as well as from the various hydrates present, and in calcareous soils of carbon dioxide, which can not be restored by treatment with ammonium carbonate, but must, if necessary, be determined in a separate portion and properly deducted. The combustible portions of the soil farther consist of two distinct portions; namely, humus ready-formed,

and unhumified vegetable matter; so that even if we were able to segregate the water belonging to the several hydrates, we would still be unable to estimate the true humus contents. This can only be done by the method of Grandeau; *viz.*, treatment of the soil first with weak acid and then, after washing, with weak ammonia water, evaporating the filtrate and igniting the residue. The methods of wet or dry combustion usually prescribed for humus determination yield results varying widely with the season, and incapable of serving as the basis of general conclusions; since it is quite uncertain whether or not the unhumified matter will ever become humus, or will be eliminated (as is largely the case in the arid region) by eremacausis, or (in the humid region) by fermentation.

In the ash of the humus, at least phosphoric acid should always be determined, since the phosphoric acid thus contained is certainly more available to plants than that not dissolved in the Grandeau treatment, although not as fully so as was at first claimed by Grandeau. The bulk of the humus ash is usually silica, which should be weighed, since we thus gain an idea of the amount of other ingredients contained in the "*matiere noire.*" But ordinarily I do not consider a farther prosecution of this analysis as of material practical importance.

The humus percentage gives an approximate idea of the nitrogen stored in the soil, the percentage of nitrogen in the "*matiere noire*" being usually three to five per cent. While this is true for the region of summer rains (the "humid"), it seems that in the arid region the nitrogen percentage in the humus is so much greater, that a direct determination alone can serve the purpose. This is readily done by substituting in the Grandeau process a solution of potash or soda for that of ammonia, and after neutralizing the filtrate, evaporating and determining the nitrogen by the Kjeldahl method.

The direct determination of nitrates and ammonia in soils is in my view usually of little interest for general purposes, outside of the arid region, where these compounds remain wholly or partially in the soil and may accumulate to a considerable extent. In the humid region they are usually present in such minute proportions and subject to so much change from day to

day, that for the purpose of judging the soils' general resources in nitrogen such determinations are of little use. When made they should, of course, be done by leaching with water and treatment of the filtrate, since we have no method by which the determination can be made in the whole soil without attacking also the nitrogen of the humus.

The determinations mentioned are in my view all that is usually called for in the examination of soils for practical purposes; very commonly, a general knowledge of the soils of a large region may render a goodly proportion of the determinations unnecessary. Thus the soils derived from the great eruptive sheet of Oregon and Washington have proved to be so universally rich in phosphates, that even this important determination frequently becomes superfluous; and almost the same can be said for potash and lime throughout the arid region. In a large number of cases it is only necessary to identify the soil under examination by mineralogical analysis with others of the same type previously examined from the same region; and this identification naturally carries with it the conclusions previously deduced from observation in the field and laboratory, with very little trouble.

It now remains for me to consider briefly what are the conclusions and practical deductions legitimately flowing from such work as I have outlined. I have heretofore published some detailed discussions of this subject, and will therefore not go into illustrative details, for which I refer to those publications.

What practical meaning shall we attach to the percentage data found by analyses made as described above? How much of each of the important ingredients must be present in order that the soil may be considered "rich" or "poor?"

In this general form the question is unanswerable, as is shown by the comparison of even a very few soils noted for great and lasting productiveness. Manifestly, cultural experience alone can answer the question in *any* form and it is precisely upon such experience that I have based the general rules I shall enunciate—not *ex cathedra*, but purely as the result of extensive *comparisons of the results of chemical analysis of virgin soils with cultural experience.*

(1) There is one invariable rule as regards plant food percentages, to which in virgin soils I fail to find a single exception. It is that all having high percentages are highly productive, unless physical conditions render them uncultivatable.

(2) The reverse is by no means generally true, for there are soils having what must be considered very low percentages that nevertheless prove both immediately productive and of considerable durability.

At first blush this admission seems fatal to the claims of chemical soil analysis to practical utility. It certainly proves that such analysis is not to be relied upon, *alone*, to determine the quality of a soil; it must be supplemented by other data than the plant food percentages.

When we discuss the cases forming this class of apparent contradiction, we find, first, that the soils so circumstanced are almost invariably rather coarsely sandy ones, and of considerable depth. So soon as we throw out of consideration the great mass of obviously inert material and examine the "fine earth" corresponding to the grain sizes of rich clay soils, our percentages assume quite a different magnitude, particularly when the great depth to which plant roots can exercise their vegetative functions in pervious soils are taken into consideration.

Three other conditions must, however, be fulfilled in order to render such soils of low percentages thrifty; namely, the *ratios* of the several ingredients among themselves must not fall below certain values. In following up the investigation of these ratios, the substance which assumes commanding importance is *lime*. Unless lime is present in sufficient proportional amount to insure the presence of a certain proportion of calcium carbonate at all times, the soil will lack thriftiness; and this is true of all soils, whether of high or low percentages. Moreover, it is strikingly true that the percentage of lime required to fulfill this condition is decidedly higher in clay soils than in sandy ones.

The existence or absence of this important condition is in general readily recognizable by the vegetation characterizing calcareous soils; and one of the first points that must strike the observer is that "lime plants" are, almost throughout, those

upon which old farmers base their successful locations of good land. But in following up this indication we soon find that we must abandon the definition of calcareous soils usually given in text-books ("soils that effervesce with acids"); for all the advantages of calcareous soils are secured with percentages of lime far below those in which the slightest effervescence can be perceived. Here, then, soil analysis renders the essential service of enabling us to account for the choice made by experienced frontiersmen and land experts; practically, *they are in quest of calcareous lands!*

That "a limestone country is a rich country" is an old adage, easily verified by any one who observes the geological map as he travels. But the adage holds true not only of limestone districts, but also of those which from other causes have a notable proportion of lime in their soils. The most striking example of the latter class is the entire arid region, of America as well as of Asia and Africa. As I have more elaborately shown in a special treatise (A Report on the Relations of Soil to Climate; Bulletin No. 3 of the U. S. Weather Bureau), the presence of a notable amount of calcium carbonate in the soils of arid countries is the necessary result of the failure of the scanty rain-fall to leach out the water-soluble products of the weathering process; foremost among these, calcium carbonate is accumulated even where no limestone formations exist. According to the adage above quoted, then, arid countries ought to be rich countries. History shows this to be true, with the proviso that there is any soil at all; for the slowness of the weathering process in arid climates renders soil formation correspondingly slow. Arid climates, moreover, necessitate irrigation; but where, as in Egypt and India, the needful water is supplied, the soil proves almost inexhaustible. It need hardly be mentioned that alongside of lime, other important ingredients accumulate in the soils of the arid regions; notably, *potash* and *nitrates*.

The good results of the presence of much lime in soils, about which there can be no practical question, is doubtless connected partly with the effects which must be attributed to calcium carbonate in the soil as well as in the laboratory: It acts in the "Aufschliessung" of silicates, and it is doubtless from this

cause that (as was mentioned above) we find such large amounts of soluble alumina in calcareous clay soils. Moreover, lime favors *nitrification*, and prevents the formation of injurious *acidity*. That much we can say with certainty; but it has doubtless other important functions, even in a chemical point of view; while as a flocculator of clay it performs a most important physical office, in promoting easy tillage, and circulation of water.

In very sandy soils, as little as 0.10 per cent. of lime may cause the soil to show "lime vegetation;" while in very heavy clay soils, I have known even 0.6 per cent. to be inadequate for this purpose. But apart from the most extreme cases, I find we may safely augur favorably of any soil containing *as much lime as potash*.

The average ratio of the lime percentages of soils in the arid and humid regions I find to be about twelve to one, if we exclude from comparison, on both sides, limestone soils proper. The most general expression I can give to the results of my discussion of the analyses of virgin soils with respect to lime, is that in its presence (in adequate proportions) much smaller pecentages of the other plant foods will suffice for high and lasting productiveness; and that much less lime suffices to produce this effect in "light" than in "heavy" soils. It thus appears, then, that the question of the adequacy of plant food percentages is largely dependent upon the proportion of lime, as well as upon the physical character of the soil. The latter point depends essentially, of course, upon the greater facility with which an extended root-development occurs in light than in heavy soils.

I think that the failure of agricultural chemistry to recognize as fully as it deserves the extreme importance of lime in soils, is measurably due to the accidental fact that partly extended limestone formations, partly the prevalence of the mixed glacier drift over the greater part of Europe and Eastern North America, have made calcareous soils so predominant in the regions where agricultural science has been developed, that the exceptional and relatively unimportant non-calcareous areas have escaped attention.

As regards *potash*, the comparisons I have made of hundreds

of analyses from the arid and humid regions of the United States, respectively show that potash, like lime, accumulates to a remarkable extent in the soils of the arid climates, doubtless in the form of zeolitic compounds; the average proportion in the two regions being about one to three in favor of the arid. Coupled with the fact that there, potash salts are often abundant in the soil water, as well as in the waters of the streams serving to irrigate these lands, the conclusion that potash is not likely to be soon called for as a fertilizer in that part of the continent becomes natural, and is abundantly confirmed by all tests thus far made. The invariable presence of an excess of lime in the arid soils, moreover, promises the current setting-free of potash from the soil zeolites.

The general average of potash in the arid soils is from 0.7 to 0.8 per cent.; for the humid soils of the Cotton States, from 0.21 to 0.25 per cent. No wonder that, considering the frequent deficiency in lime in the latter region, the Stassfurt salts are among the first of the effective fertilizers for the Eastern United States.

As regards *phosphoric acid*, the comparison of the soils of the humid and arid regions fails to reveal any constant difference; its presence in larger or smaller proportions being, apparently, dependent entirely upon local geological and petrographic conditions. It is curious that in my investigations of virgin soils I have been led to the identical figure for the minimum percentage of this substance that will still insure profitable culture, that, I find, has been accepted by European investigators; namely, five-hundredths of one per cent. (0.05 per cent.). When no more than this amount is found to be present in any soil, production will soon cease unless phosphatic fertilizers are used; the duration of profitable culture depending materially, however, upon the proportion of lime present. Anything much above one-tenth of one per cent. usually proves, in virgin soils, to be quite a full supply, rendering the use of phosphates ineffective for a number of years.

Owing to the difficulty formerly existing in the *nitrogen* determination in soils, my investigations in this direction have not been as extended, nor the results as conclusive, as in the case of

the mineral ingredients. Taking the humus determined according to Grandeau as an approximate gauge of the nitrogen store in soils, it would seem that in the humid region—the Cotton States in particular—less than 0.5 per cent. of humus, estimated to contain say an average of five per cent. of nitrogen, constitutes a deficiency; while in the arid region, as before noted, less than half that amount seems to suffice, rendering the use of nitrate fertilizers ineffective. But owing to the faultiness of the methods employed, the data thus far existing are, as yet, too scanty to serve profitably for the discussion of these points.

In summarizing the outcome of my studies on the relations of the actual productiveness of virgin soils to their plant food percentages, I might say that they support the intrinsically reasonable general thesis that *the amount of available plant food in virgin soils of essentially similar origin is sensibly proportional to the respective totals of such ingredients found by analysis;* provided we take into consideration both the proportions of these ingredients among themselves, and the physical nature of the soil. It is abundantly evident that sandy, pervious soils can, owing to the greater root-development they permit, be fertile with much smaller percentages than those which are difficult of penetration; at the same time, there is an obvious limit beyond which this greater root surface cannot make up for too great a scarcity of one or several ingredients. The test of how far the dilution of a close, fertile soil with pure sand can be carried without detriment to production, is apparently easy to make; and yet these experiments encounter no inconsiderable difficulties in actual execution. Yet their importance is so fundamental that I propose to prosecute them as diligently as circumstances permit, and earnestly hope that others will work in the same line of research.

HYDROGEN SULPHIDE GENERATOR.

By H. A. Bishop.

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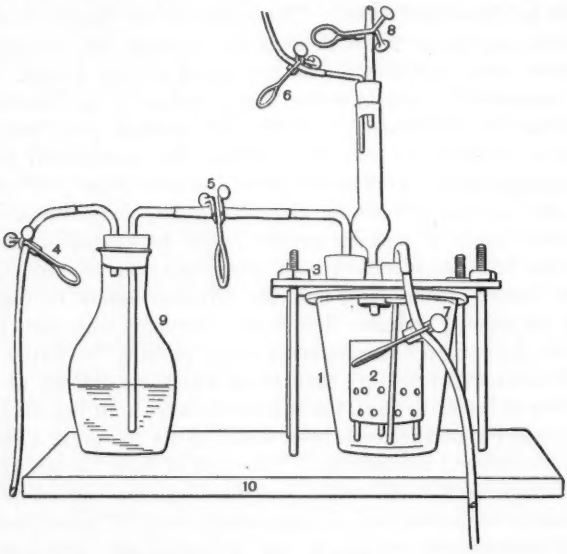
THE accompanying figure represents a very useful contrivance for the generating of hydrogen sulphide. It consists of 1, an ordinary glass tumbler placed upon a wooden base 10. 2 is a leaden cylinder pierced with small holes. Between



1 and 3 is a rubber washer which makes the generator complete when 1 is held in place by four bolts as seen in the figure, 9 is a wash bottle. When iron sulphide has been placed in 2, the apparatus is ready for generating hydrogen sulphide, first by opening first cock 4, then 5, and finally 6, which allows the acid to enter 1, from a supply receptacle. When the acid has risen above the holes in 2, 6 is closed and all is in operation. After sufficient H_2S has been obtained 4 is closed first, then 5, and 7 is opened after which 8, which is connected with a water bottle which allows water to wash out what acid remains. The working and construction is very simple.

THE USE OF ELECTROLYSIS IN TECHNICAL CHEMICAL PROCESSES.[1]

By J. W. Langley, Cleveland, Ohio.

TECHNICAL chemistry covers a very wide field stretching from metallurgy on one side to the production of the most delicate colors and odors on the other, in all of which, possibly, electricity is destined to play a part although up to the present time it has only been used to any important extent in the division including the chemical side of metallurgy. Here by far the most notable examples of its use are in the purification of copper and in the extraction of aluminum.

The electrolytic separation of pure copper from crude copper is substantially only a large expansion of the old processes of electrotyping and electroplating, and therefore does not offer much which is novel, but the production of aluminum from its oxide is a typical example of an electro-metallurgical operation. I propose, therefore, to describe somewhat in detail the method employed as it will serve to indicate the steps and precautions to be observed in the applications of electrolysis to other metallic compounds.

The electrolytic production of aluminum is an industry only five years old, but in that short period it has completely revolutionized the manufacture of this metal; indeed it is to-day the only successful method and will probably remain for a long time without a competitor. In this country the process is carried on only by the Pittsburg Reduction Company, at New Kensington, Penna., which manufactures under broad patents granted to Chas. M. Hall, the discoverer and patentee of what is now generally known as the Hall process.

The very important discovery which is the foundation of this method is the fact that oxide of aluminum is soluble in certain double fluorides in a fused condition; the salt which operates the best for this purpose must be composed of fluoride of aluminum and of a fluoride of a base more electro-positive than aluminum; sodium, potassium, and lithium fulfill this condition, but on account of expense fluoride of sodium is preferred. The

[1] Read before the World's Congress of Chemists, August 25, 1893.

mineral cryolite $Al_2Na_6F_{12}$, or as it may also be written $Al_2F_6(NaF)_6$, is a native fluoride coming within the requirements of the class of double fluorides necessary and it forms the principal solvent used. Only, as its melting point is somewhat high, it is an advantage when not operating on a very large scale to add to it small amounts of other fluorides to bring down the fusing point.

Cryolite will dissolve more than twenty-five per cent. of its weight of alumina forming a clear and colorless solution from which the metal can be readily electrolyzed.

There are some features of theoretical interest about this act of solution, for that it is a solution rather than a chemical compound there can be no doubt. Alumina when added to the melted salt dissolves quietly without effervescence or any manifest evolution of heat, resembling in all respects the solution of salt or sugar in water. But alumina is not appreciably soluble in melted sodium fluoride, and aluminum fluoride by itself is infusible except at extremely high temperatures. The presence of both fluorides is absolutely essential. The two fluorides may be taken initially as a double salt or they may be separately mixed with alumina, the final result is the same; *viz.*, the perfect solution of the oxide.

The electrolytic decomposition of the dissolved oxide is carried out on a manufacturing scale by using carbon electrodes. A rectangular vessel made of iron-boiler plate is lined with compressed carbon to a thickness of from four to six inches. This constitutes the negative electrode; the positive electrode is formed of carbon rods three inches in diameter by twelve in length, suspended by copper rods from a horizontal copper arm above the iron vessel. The number and disposition of these carbon anodes depend on the scale of the operation. They are hung so that they will terminate about one inch from the carbon lining, and the purpose of suspending them is that they may be easily removable one or two at a time without stopping the whole current going through the apparatus.

The iron vessel is called the pot. The melted cryolite the bath, or when it holds alumina in solution is often termed the electrolyte.

To start the operation some powdered cryolite or the mixture of double fluorides is placed on the carbon lining which is cold. The carbon anodes are then lowered till they make contact with the lining, much local heat being at once produced partly by the resistance of the carbon at the points of contact and partly by numerous short arcs formed where apposition is not perfect. This heat soon melts some of the bath material which flowing between the electrodes adds its own resistance thereby increasing the heat because there is now a larger cross section of conductor and consequently more current carried. In this way the bath material is fused and the pot finally filled. The pot may also be initially charged with melted cryolite ladled into it from a separate melting pot.

During this period while the bath mixture is fusing electrolysis is necessarily going on but it yields only a small quantity of aluminum, probably because of the access of the air and also because any fluorine potentially or actually liberated finds some of the metal in a finely divided and diffused condition with which it reunites.

When a sufficient volume of melted bath is secured the second or permanent stage of manufacture begins, powdered alumina is spread over the top of the bath and periodically stirred down into it. It dissolves almost immediately and normal electrolysis takes place. Aluminum is deposited in a melted condition at the bottom of the bath against the negative electrode, while the oxygen which is transferred to the positive side burns the anodes escaping as carbon monoxide and carbon dioxide. The anodes are thus consumed and must be from time to time pushed down further into the bath. The melted fluorides are not electrolyzed and may be used over and over again indefinitely, it being only necessary to add enough to supply the small losses principally of a mechanical nature occasioned by the removal of the metal. The operation is strictly continuous, alumina is added on the top of the bath and the metal is ladled out from the bottom.

There is quite a complicated adjustment of chemical and electrical forces concerned in the successful electrolysis of alumina which are interesting from the standpoint of pure science.

The current employed by the Pittsburg Reduction Company is 7000 amperes. In order to send this through a bath of melted fluorides only, with the usual current density requires fifteen volts, but as soon as alumina is added the pressure promptly falls to from six to seven volts which is that necessary for the normal working of the process. This E. M. F. is obviously consumed in two ways: First, by the force of polarization necessary to break up a molecule of Al_2O_3; second, by the fall of potential due to the resistance of the anodes and of the bath. It is possible to calculate this work both in chemical and in electrical measures.

The heats of formation of one molecule each of the bath constituents is as follows:

Sodium fluoride	109,700 calories
Aluminum fluoride	550,000 "
Aluminum oxide	388,920 "

The electromotive force of decomposition depends, as is well known, on the equivalent and not on the molecular weight and these will be $Al_2O_3 = Al_2F_6 = 6\,(NaF)$.

The energy of 22,900 calories is proportional to one volt, according to Sir William Thomson, therefore the E. M. F. of decomposition will be:

Sodium fluoride	$\frac{109700}{22900} = 4.8$ volts
Aluminum fluoride	$\frac{550000}{22900 \times 6} = 4.0$ volts
Aluminum oxide	$\frac{388920}{22900 \times 6} = 2.8$ volts

Thus the oxide of aluminum is the weakest body present and the only one to be decomposed provided the current density is not permitted to become too great.

The fact that no appreciable quantity of fluorine is given off, but only oxygen, when the pots are working at normal voltage and current is perfectly explained by the above theoretical values of the electromotive force of decomposition. The direct measurement of this force presents considerable difficulty on account of the variation of the resistance of the bath with its temperature, but the best estimates from actual measures show that the breaking stress of one-sixth of a molecule of alumina is certainly less than 3.5 volts. Thus the theoretical number is fairly well sustained by practical observation.

The fundamental conditions for the successful electrolysis of any metallic compound are then these: First, the metallic salt must be in the fluid state; second, if it is rendered fluid by a solvent then the electromotive force of decomposition of the salt must be less than that of the solvent; third, the current density must be carefully regulated. These statements apply equally to aqueous solutions and to baths rendered fluid by fusion. The double fluorides would seem to be the only substances which can fulfill these conditions on a commercial scale for aluminum.

The theoretical equation of the decomposition of alumina by carbon is

$$Al_2O_3 + 3C = 2Al + 3CO$$

which would require about two-thirds of a pound of carbon for each pound of metal produced. Now, in the electrolytic process one pound of carbon anodes is lost for each pound of metal, the slight excess over theory being due to some combustion of the carbon by the air above the surface of the bath. The yield of metal is one pound of aluminum for 18.1 electrical horse power hours. This energy, it must be remembered, is spent both in causing decomposition and in maintaining the temperature of the bath, which is about that of the melting point of copper.

Taking the voltage of the baths as 7, then 18.1 electrical horse power hours represent a continuous flow of 1,926 amperes for one hour. This would theoretically deposit 1.43 pounds of aluminum, so that the actual yield is seventy per cent. of the theoretical ampere production. This must be considered fairly satisfactory. Of course the yield calculated on the total energy consumed is considerably less than this, owing to the large fraction which is turned into heat; but this loss must be set over against the consumption of fuel in ordinary metallurgical work where it is burned solely to produce heat.

Another example of the application of electrolysis to an important industry is the refining of gold and silver, but more particularly silver. The practical details as carried out by the Pennsylvania Lead Company, of Pittsburg, Pa., under the Moebius process are as follows:

Tanks are made and divided into compartments so that they may be connected up in series. The unit compartment is 18″ x 24″ x 17″ deep, and seventy of these are in the circuit at one time. Each compartment has three anodes, 10″ x 20″ x ½″, and four cathodes of about the same area as the anodes. The anodes are composed of the metal to be refined which will average 990 fine in silver, the rest being mainly copper, lead, bismuth with a little gold. The cathodes are thin sheets of pure silver. The surface exposed in each compartment, reckoning both sides of the plates, is twenty square feet, or 1,400 feet for all the tanks. The anodes are hung in a bag to catch the insoluble material which drops from them. The electrolyte is a dilute nitric acid as free as possible from sulphuric acid or chlorine. A current of 180 amperes is used and the voltage required by each compartment is 1⅓ volts. The consumption of nitric acid (36° B.) is about two pounds per day for each compartment. The amount of silver deposited is, in practice, about 470 ounces per twenty-four hours in each compartment, which is equal to 1.35 pounds avoirdupois per hour. This includes all interruptions of current for all reasons. The total amount of silver refined per day is 32,900 ounces, or practically one ton. This is eighty-four per cent. of the theoretical yield for 180 amperes working the same length of time without any interruption whatever. The product is practically silver 1000 fine.

The success of this operation depends evidently on the difference of the electromotive force of silver against nitric acid, and of copper, bismuth, and lead against nitric acid, silver being the lowest. But the difference between silver and copper is not great, and a very careful regulation of current density is necessary, which, however, can be attained, making this method one of the neatest applications of electro-metallurgy and one which replaces the tedious cupellations necessary by the older process which has come down from the middle ages.

Another application, which is wholly chemical, has recently been made to the purification of sewage near New York.

Many attempts have been made to produce caustic soda and chlorine, or bleaching compounds, from common salt by electrolysis; but thus far they have not advanced to the stage of

industrial success. One of the chief reasons for this is because no insoluble anode has been discovered, for in strong solutions platinum is dissolved and carbon is oxidized and corroded; but when the liquid is weak this trouble with the anode is considerably lessened. A report by Dr. Cyrus Edson, of the Health Office, New York City, partly reprinted by the *Electrical Engineer*, gives an account of a successful experiment recently made to disinfect the sewage of the village of Brewsters which was finding its way into the city water supply. Mr. Albert E. Wolf proposed to accomplish the purification of the sewage by treating it with electrolyzed sea water. A current of 700 amperes by five volts is delivered to the water as it flows slowly past seven electrodes. Of these, four are carbon, 12″ x 12″ x 1″ thick, while the anodes are copper coated with platinum. The flow of the solution is so limited that the salt water is electrolyzed to the proper degree and then overflows from the tank directly into the sewer. The disinfection is practically perfect. Tests show that this electrolyzed sea water equals in strength a one per cent. solution of chloride of lime. In the matter of cost the treated sea water costs 0.01 cent a gallon, while a one per cent. solution of chloride of lime costs 1.4 cents per gallon, or the sea water costs only $\frac{1}{140}$ of the lime. Compared with the cost of corrosive sublimate, the latter is one hundred times as expensive for an equal efficiency, while carbolic acid costs from two to three hundred times as much.

Other applications which have been tried and are now on their way to commercial development are: Bleaching fabrics without chlorine by means of electrolyzed acidulated water only, and the tanning of hides.

Seeing that in electrolysis we have a powerful analytic force at work heaping up products of decomposition at each pole, it would be natural to look for some means to utilize the powerful oxidizing and reducing actions of which the electrodes are the foci. This would be to save and turn to useful account the secondary reactions of the cell. A careful study of the conditions under which these secondary actions are a maximum and a minimum can scarcely fail to lead to many applications of the current in technical chemical work where electricity will be

used primarily as an oxidizing or a reducing agent and only secondarily as an agent for electrolytic decompositions.

There is one great desideratum, and that is a cheap insoluble anode. Platinum is too expensive, and carbon will not long withstand oxidation. It is this lack which to-day, among other conditions, prevents electricity from being a rival to the ammonia process of making soda and to the Leblanc process for producing bleaching powder as a by-product, and to its utilization as an oxidizing agent. When the cheap insoluble anode is found it will open a wide door to the applications of electricity to the chemical arts.

[CONTRIBUTIONS FROM THE ANALYTICAL LABORATORIES OF THE SCHOOL OF MINES, COLUMBIA COLLEGE.—No. 1.]

THE IODINE FIGURE OF ROSIN.

BY PARKER C. MCILHINEY, PH.B., A.M.

Received December 9, 1893.

IN the analysis of oils, and especially drying oils, one of the most useful tests is a determination of the Hübl number. The iodine figure of rosin, which is a common adulterant of oils, is stated by Benedikt (Analyse der Fette und Wachsarten, 171) to be 115.7; Williams (*Chem. News*, **58**, 224) gives 115.31 and 114.80 for refined rosin and 112.01 and 113.28 for ordinary. Mills (Destructive Distillation, 13) has determined the bromine absorption to be 112.7 per cent., which would correspond to an iodine absorption of about 179. In order to throw some light on the causes of this disagreement, experiments were made to ascertain the effect of different amounts of iodine in excess, different times of absorption and different qualities of rosin.

Five samples were used representing different grades from "W.W." (water-white) rosin to "A" (black).

In the tests made to ascertain the influence of time and of excess of iodine the rosin used was that known as W.W., which is the best grade in the market. The iodine solution used contained twenty-five grams of iodine and thirty grams of mercuric chloride per liter, and the thiosulphate solution 24.8

grams of sodium thiosulphate per liter. The thiosulphate solution was standardized by means of a solution of potassium dichromate made from chemically pure dichromate which had been further purified by several recrystallizations. The tests were made in bottles of 250 cc. capacity, having carefully ground stoppers, such as are used in the assay of silver bullion. The rosin was in each case dissolved in ten cc. of chloroform and the absorption was effected in a dark closet.

The results were as follows:

Quality of rosin.	Quantity, grams.	Excess of iodine in cc. $\frac{N}{10}$ thiosulphate	Time of absorption.	Iodine figure.
Water-white	0.3030	17.4	2 hours.	142.9
" "	0.3017	25.4	2 "	146.4
" "	0.3048	33.2	2 "	148.5
" "	0.3010	50.2	2 "	152.1
Water-white	0.3007	13.35	1 hour.	126.7
" "	0.3027	11.6	2 hours.	133.1
" "	0.3003	10.5	4 "	142.0
" "	0.3023	8.8	8 "	144.8
" "	0.3087	11.55	18 "	160.3
" "	0.3033	1.9	52 "	172.6
"A" (black)	0.3055	20.25	18 hours.	143.6
"E"	0.3012	14.2	18 "	156.4
"G"	0.3054	13.7	18 "	153.1
"W.G." (window-glass)	0.3160	9.7	18 "	164.2
"W.W." (water-white)	0.3087	11.55	18 "	160.3

It appears from these results that the average iodine absorption in eighteen hours by different qualities of rosin is 155.5, the average quantity of rosin used being 0.3073 gram and the average excess of iodine equivalent to 13.88 cc. $\frac{N}{10}$ thiosulphate. The darker samples of rosin absorb less iodine than the lighter ones which have been subjected to less heat. The variations due to different lengths of time and different amounts of iodine in excess are, however, so serious that comparatively little can be learned by Hübl's process as to the nature of an oil when rosin is present in any considerable quantity.

AN IMPROVED FILTER-DISK.[1]

By Max Kaehler.

AN obstacle to the extended use of the porcelain filter-disks, introduced by Otto N. Witt, (*Ber. d. chem. Ges., 1886*, 918), has existed in the great difficulty of securing a uniformly tight joint between disk and funnel. On the one hand it was necessary to have funnels whose walls were not only perfectly smooth, but were inclined at an angle of exactly 60°. On the other hand any irregularity on the side of the disk seriously affected the tightness of the joint, and frequently, even when the oblique position was scarcely evident to the eye, caused the cracking of the funnel.

These difficulties have been overcome by the introduction of a modified form shown in the accompanying sketch. The disks are made with a rather deep groove running around the side, in which is held a stout rubber ring (c), projecting a slight distance beyond the adjoining surface. The disk is further perforated in the center by a funnel-shaped opening, into which is adjusted a glass rod (a) which extends down into the neck of the funnel. The rubber ring produces a perfect joint while the glass rod keeps the disk in a horizontal position. When large disks and wide-necked funnels are used a cork with channeled sides and fitting closely in the funnel's neck is slipped over the lower end of the glass rod.

[1] Read before the Cincinnati Section, December 15, 1893.

The new device assures rapidity and certainty in manipulation with complete absence of danger to the funnels employed.

These new disks are manufactured by Kaehler and Martini, of Berlin, Germany.

QUANTITATIVE WORK FOR BEGINNERS IN CHEMISTRY.[1]

By W. A. Noyes.

IN most of our chemical laboratories the work which is given to beginners is chiefly or altogether of a qualitative nature. In many schools and colleges the work begins with a study of the qualitative properties of a series of chemical elements and their compounds, chiefly of gases and metalloids. In other schools the students begin at once with the study of qualitative analysis. A large majority of our students never get beyond this first stage and it is safe to say that they acquire but a very slight knowledge of real chemical work. The work which is done in our scientific and technical laboratories and in chemical factories consists almost entirely of quantitative analyses or of the preparation of chemical substances carried out in an accurate quantitative manner. Indeed, we are accustomed to say that the science of chemistry began with the use of the balance and we all recognize the extreme importance of quantitative relations in most of our chemical work.

We must keep in view several objects in selecting the laboratory work for beginners. First they should become personally acquainted with the appearance and properties of a number of the chemical elements and their compounds. The acquisition of a large amount of knowledge of this kind is desirable but we may easily make the mistake of endeavoring to impart too much. A few topics exhaustively studied will prove of greater value than a superficial study of a great many. This is especially true of qualitative tests with solutions. A beginner can apply a great many such tests in a comparatively short time, but unless his powers of discrimination and of memory are very unusual he will retain only a confused recollection of his work. A second object is to secure a training in delicate and accurate manipulation and in the use of different forms of apparatus. A third

[1] Read before the World's Congress of Chemists, August 26, 1893.

object is to fix in the mind of the student knowledge which may have been imperfectly acquired by watching the demonstrations of a lecturer or by the study of a text-book. Some teachers carry this thought so far that they seem to imply that no knowledge of a topic can be really acquired by the student until he has demonstrated it by personal experiment. Indeed I have heard some teachers contend that they would not allow a text-book in the laboratory, but would have their students acquire all of their knowledge at first hand by their own experiments. Such a principle if logically carried out could never take the student beyond the stage of alchemy, for the student of to-day is no better able to develop a science of chemistry for himself than was the old alchemist. And if you direct his experiments in such a way as to develop and elucidate the science as it is now known, you have forsaken the principle just as much as though a text-book were used.

It seems to me that such views arise from a mistaken conception of the real nature and purpose of laboratory instruction. After all, the method of personal experiment is a very slow and laborious method of acquiring knowledge. Only a very small fraction of our knowledge of a science, if that knowledge is by any means adequate, has been acquired in that way. It is true that the method is absolutely essential for beginners, and I do not think that any of us get beyond the need of it. The man who never uses a balance or handles a test-tube will not for very long be a strong factor in the advancement of chemical science. But the method of laboratory instruction is essential, not because knowledge can not be acquired in other ways, but because at the start the imagination of the student is deficient and it is only by means of personal experiments of his own that he can acquire the ability to understand and appreciate the experimental work of others. The memory is also deficient and the personal work on a subject may be of great value for that reason, as well. But the things which we should endeavor to secure in laboratory instruction are, first, such an acquaintance with experimental methods as shall enable the student to thoroughly grasp the solid experimental basis of the science and give him the mental habit of referring everything back to the rigid ex-

perimental test; and second, the ability to do accurate and independent experimental work himself. No student can demonstrate for himself more than an infinitesmal number of experimental facts in comparison with the vast array of such material which has been accumulated.

If the principles which I have suggested are correct we should endeavor to secure as thorough a knowledge as possible of experimental methods, and neatness and accuracy in laboratory technique rather than the illustration of as large a number of details as possible. These results can be secured more fully by a series of quantitative problems than by a large amount of merely qualitative work. I do not mean by this that qualitative work is not necessary and desirable as well, but for the beginners, especially, quantitative work is of more value. In order to make my meaning more clear I will give a few illustrations. One of the earliest problems that I give is the determination of the weight of a liter of hydrogen essentially by Regnault's method. A bulb containing about one-half a liter and bearing a three-way cock is exhausted with a Bunsen pump and the residual pressure determined with a manometer. The bulb is then weighed, using a sealed counterpoise of nearly the same volume, then filled with hydrogen, temperature and pressure noted, and weighed again. The results obtained by careful work are usually one or two per cent. too high. A similar determination of the weight of oxygen gives results with a far smaller percentage error. The determination of the amount of oxygen in potassium chlorate by heating about a gram of the salt in a small porcelain crucible placed within a second gives a good illustration of the law of constant proportion. The preparation of potassium perchlorate can be made to furnish a considerable amount of valuable instruction. The capacity of a bottle holding about two liters is determined, a calculation of the amount of potassium chlorate required to give oxygen enough to fill it when only the first stage of the reaction is used, is made and the experiment performed. Then the potassium chlorate and potassium perchlorate are separated and the latter is purified by crystallization. A study of the qualitative reactions which distinguish potassium chloride, potassium chlorate and potassium perchlorate

is made and the tests to establish the purity of the last are applied. Finally a determination of the amount of oxygen in potassium perchlorate gives, in connection with the last problem, an illustration of the law of multiple proportion. I will give but one further illustration—the determination of the relative atomic weights of hydrogen, chlorine, and silver. A known weight of pure silver is dissolved in nitric acid, precipitated with hydrochloric acid and the silver chloride weighed on a Gooch crucible. In a dilute hydrochloric acid the amount of hydrogen is determined by allowing ten cc. of it to act on an excess of zinc in an appropriate apparatus, the hydrogen being measured in a gas burette, accurate corrections being made for temperature, pressure, and aqueous pressure. In another known volume of the same acid the chlorine is determined by precipitation with silver nitrate.

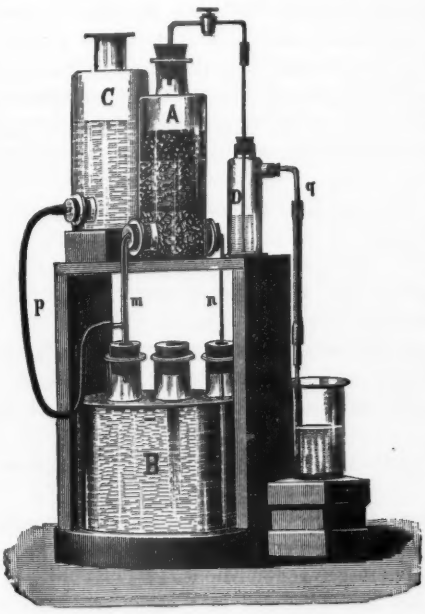
By a careful selection of problems it is possible to give the student, within a reasonable time, practice in the careful use of the more common forms of chemical apparatus. In other words the student can make a beginning at working as a chemist works instead of doing scarcely more than play with bottles and test-tubes. Among other advantages of this method of instruction is the fact that the results which are obtained are usually a fairly good criterion by which to judge of the care with which the student has worked, and the student soon finds that careless work will not give good quantitative results. Also the student dwells long enough on a problem so that many details become thoroughly fixed—a result that is rarely obtained in qualitative work, except by means of many repetitions. I am aware that there are some practical difficulties in the way of carrying out the methods which I propose, especially in the matter of apparatus, but these difficulties are not nearly so great as they appear at first sight and I am sure that they are not greater than those which have been overcome in many of our physical laboratories.

A NEW HYDROGEN SULPHIDE GENERATOR SPECIALLY ADAPTED FOR USE IN ANALYTICAL LABORATORIES.[1]

By L. L. de Koninck.

THIS new form of generator has yielded such excellent results, especially in connection with quantitative work, where the need of a constant, easily regulated current of hydrogen sulphide is so often felt, that a detailed description of its construction and handling is now made public.

The arrangement of the different parts is shown in the accompanying cut, in which A, the generator proper, rests upon a wooden support. It consists of a large wide-necked bottle, provided at the lower part with two tubulures, opposite one another. The bottom is covered with a thick layer of broken glass or porcelain. A three-necked Woulff's bottle, B, of ample size, but low form, is placed beneath the wooden support. The tube n passes from A to the bottom of B. The T tube m passes likewise from A to B, but terminates immediately beneath the stopper, while its branch is connected by means of rubber tubing p, with the tubulure of the movable pressure bottle C. The outlet tube of A, provided with a glass



[1] Read before the Cincinnati Section, November 15, 1893.

cock, enters the wash-flask D, from whence gas can be directed at will through q. The middle neck of B can be used for the introduction of a siphon in charging or emptying the apparatus.

The method of using the apparatus is exceedingly simple. A receives a full charge of iron sulphide. B and C are filled with acid, and the latter placed upon a block at the proper elevation. When the cock above A is opened the acid flows into A, the generation of hydrogen sulphide begins, and the gas streams out through the wash-bottle D. As ferrous chloride forms in A, its solution on account of its greater specific gravity sinks continually downward through n, to the bottom of B, while fresh acid enters to take its place. A circulation is thereby established first of strong acid and then of acid containing gradually increasing amounts of ferrous chloride, until the point is reached where nearly the entire stock of acid is changed into ferrous solution. The rapidity of the liberation of the gas can be controlled by raising or lowering C, as well as by the adjustment of the cock in the outlet tube. The current is stopped by lowering C and placing it along side of B, but so that its neck is higher than those of B.

From the above the following advantages of this new apparatus will be easily understood:

1. The current of gas is uniform throughout a given operation, standing under a pressure of 20–30 cm. of water, and capable of being regulated at will.

2. When not in use the pressure is removed and there is no possibility of wasting material either by accident or otherwise.

3. A practically complete utilization of the acid employed is attained.

4. The parts of the apparatus are simple and easy to replace in case of breakage.

It is, of course, evident that the apparatus can be charged with marble or zinc and used to generate carbon dioxide or hydrogen under the same advantageous conditions.

The complete apparatus is constructed in a satisfactory manner by the well-known instrument manufacturers, Max Kaehler and Martini, of Berlin.

LABORATORY NOTES.

By James S. de Benneville.

Received December 7, 1893.

BERYL.

In determining the alkalies in a beryl from Fahlun, Sweden, the percentage of potash seemed worth noting. In the analyses of beryl accessible to me I find potash put down as one of the constituent alkalies but undetermined. (J. S. Diller, Hillebrands Min. Notes, Bull. 55 U. S. Geol. Survey in the case of a white beryl from Winslow, Me.) F. C. Robinson, (*J. Anal. Appl. Chem.*, **6**, 510) in a beryl from near Yarmouth, Mass., also notes the presence of phosphoric acid. Beryl from the localities noted in *Dana's Mineralogy*, sixth edition, do not give this alkali. In making the examination the platanic chlorides of cesium (when present) and potassium were boiled with small portions of water until the cesium lines appeared sharply in the spectroscope. The potassium salt was subsequently examined for cesium, with negative results. Other specimens of beryl were then examined and all were found to contain notable quantities of potash. The only contamination appeared to be a little ferric oxide. Nos. I, II, and III, were given to me by the late Dr. F. A. Genth to whose kindness I owe not only the specimens but the constant advice and supervision he gave so freely to those studying under him. No. IV was obtained from Geo. L. English and Co., of New York.

Analyses gave:

I. Fahlun, Sweden, dull yellow. In small grains. Sp. gr. 2.713.

II. Black Mt., Buncombe Co., N. C., apple green. Vitreous. Manganese trace. Sp. gr. 2.748.

III. Acworth, N. H., light green. Vitreous. Sp. gr. 2.714.

IV. Acworth, N. H., light green. Vitreous. Sp. gr. 2.730.

	I.	II.	III.	IV.
SiO_2	64.02	66.24	65.23	66.53
Al_2O_3	16.44	17.64	17.72	17.11
Fe_2O_3	0.68	1.36	1.35	0.94
BeO	12.91	11.06	12.37	12.24

	I.	II.	III.	IV.
MgO	0.23	0.09	0.37	0.20
CaO	0.50	0.36	0.61	0.43
K_2O	2.76	0.30	0.35	0.22
Cs_2O		. .	. .	0.12
Na_2O	0.25	0.60	0.53	0.97
Li_2O	0.05	0.14	0.06	0.17
H_2O	1.76	2.06	1.49	1.49
P_2O_5	0.26	0.78	0.14	trace
	99.86	100.63	100.22	100.45

COPPER ANALYSIS.

Experiencing considerable trouble in analyzing, for the minor constituents, pig copper and copper alloys high in copper content, a method was sought by which the great mass of the predominant constituent would remain in solution and the elements present only in small quantities would be concentrated in a precipitate of comparatively small bulk and corresponding ease in handling, the use of separate portions of the same sample for the determinations being avoided as far as possible. The method given below is based on a number of experiments conducted with the view of ascertaining the solubilities of the salts involved, under the conditions in which they would occur in analysis of a pig copper and alloy and in analyses of copper containing known quantities of the elements usually found in commercial products.

Ammonia alone being uncertain both in completeness of precipitation and from the tendency of the precipitate to run through the filter, the following modification was adopted for systematic examination of such alloys and was found to remedy the drawbacks above mentioned:

Ten grams of copper were dissolved in nitric acid. Any great excess of acid removed by evaporation. Ammonia added to resolution of the copper salt. Barium hydroxide added in excess of the quantity sufficient to precipitate the minor constituents sought. Excess is quickly indicated by the separation of a scum of barium carbonate. Filtration was made in about half an hour. The precipitate separates out rapidly. Wash well with dilute ammonia to remove any adhering copper salt. With ten grams

of copper and a dilution of 150 cc. but little copper ammonium salts separated out. Fifty grams of copper and a dilution of 500 cc. gave on standing a considerable quantity of the salts. They are, however, readily soluble in dilute ammonia on warming, the precipitate not being appreciably so. On account of the dilution the method is only qualitative for arsenic and phosphorus. For lead, bismuth, tin, iron, manganese, and antimony it is complete. Silver, zinc, and cadmium were removed from the filtrate by decolorizing with solid potassium cyanide and precipitating by hydrogen sulphide. The barium salt gives no trouble. The sulphates of lead and barium can be weighed together. The lead sulphate separated by any of the known solvents, and determined directly or by weighing the residual barium sulphate. The treatment of the precipitate containing lead, bismuth, etc., is a matter of choice.

PATENTS OF INTEREST TO CHEMISTS.

EDITED BY ALBERT H. WELLES.

Ore Separators, etc.—511,512, December 26, Crosby, G. G., magnetic ore separator. 511,162, December 19, Roberts, F. C., puddling furnace. 510,251, December 5, Giroux, J. L., reverberatory, smelting, and refining furnace. 511,476, December 26, Vattier, C., roasting furnace. 511,090, December 19, Mathewson, E. P., furnace tap. 510,223, December 5, Wohlschlegel, C., pottery kiln. 509,890, December 5, Gonder, P., brick kiln. 510,448, December 12, Smith, M. V., coke oven. 510,051, December 5, Seymour, C. E., system of concentrating ores. 510,395, December 12, Ashcroft, E. A., apparatus for generating steam by aid of molten slag. 509,912, December 5, Jory, J. H., amalgamating sluice. 511,334, December 26, Hewett, G. C., manufacture of coke by heating coal at low temperature under pressure, consolidating into lumps, and coking in an ordinary furnace.

Iron and Steel.—511,648, December 26, Parkinson, W., converting cast-steel into wrought iron, by mixing charcoal and rolling mill scrap, reducing to a spongy mass and mixing with particles of low steel and puddling. 509,973, December 5, Urick, W. P. B., method of casting solid ingots of steel. A rod is thrust into mold, then withdrawn and more molten metal is added to fill the mold. 510,340, December 5, Hines, J. H., coating iron with magnetic oxide, covering first with metal or alloy which will volatilize at a temperature below the fusing point of the iron, and then heating.

Lead.—510,979, December 19, Lunge, G., basic lead salts and caustic

alkali. Crude pig lead is oxidized and treated with nitric acid, the silver is precipitated with finely divided lead, and basic lead salts are formed by adding an alkaline carbonate and some free base. The alkaline nitrate is decomposed by ferric oxide, heated air, and steam, and the resulting ferrite is decomposed into ferric oxide and caustic alkali and nitric acid is recovered.

Copper.—**510,340,** December 5, Hines, J. H., ornamenting metal, after cleaning, by depositing copper, or aluminum and enameling.

Acids and Alkalies.—**510,900,** December 19, Cutten, E. B., electrolytic apparatus for soda and chlorine. **511,330,** December 26, Fahrig, E., process of and apparatus for obtaining ozone from the air, by absorbing oxygen, releasing the gas from the absorbent, heating, drying, cooling, and passing the electric current. **509,957,** December 5, Siepermann, W., manufacture of cyanides; alkaline carbonates are subjected to a dark red heat in presence of ammonia, and potassium cyanide is separated from its aqueous solution by increasing the per cent. of potassium carbonate or caustic potash in solution.

Sanitary Chemistry.—**510,825,** December 12, Stratton, J. L., and Murdock, F., disinfecting apparatus. **510,756,** December 12, Adam E., and Rehfuss, M. O., filter, and **510,757,** same parties, sterilizing apparatus.

Brewing and Distilling.—**510,827,** December 12, Weisebrock, F. W. A., manufacture of beer. **510,219,** December 5, Warren, M., method of and apparatus for beer manufacture. **511,353,** December 26, Mosler, J., caramel from distilling refuse.

Bleaching and Dyeing.—**511,532,** December 26, Kothe, R., *et al.*, blue tetrazo dye. **511,653,** December 26, Schultz, G., blue basic dye from alkalized paradiamins. **509,929,** December 5, Moeller M., blue azo dye. **511,688,** December 26, Diehl, T., and Moeller, M., blue-black tetrazo dye.

Tanning.—**511,411,** December 26, Dennis, M., tanning liquor, normal chromium chloride is rendered basic by adding a solution of an alkali or alkaline carbonate. **511,007** December 19, Zahn, W., tawing hides or skins, a composition of chrome alum and a sulphide of an alkali is used. **511,301,** December 19, Lawley, W. F., method for tanning hides.

Organic Compounds.—**511,303,** December 19, Majert, W., piperazine, $C_4H_{10}N_2$ anhydrous, with caustic properties, a solvent of uric acid. **511,708,** December 26, Moeller, M., amido-naphthol disulphonic acid. **511,450,** December 26, Noyes, A. A., and Clement, A. A., paramido-phenol-sulphonic acid, made by electrolyzing a sulphuric acid (conc.) solution of nitro-benzol. **510,617,** December 12, Stevens, J. H., and Axtell, F. C., compound of pyroxylin, containing pyroxylin, phenyl acetamide, acetone, and a liquid menstruum. **510,132,** December 5, Hagemann, O. C., separating tannin, dissolving tannin from substances containing it in amyl alcohol and separating the alcohol. **511,143,** December 19, Higgin, W. H., manufacture of sodium acetate from "esparto liquors," by evaporating water, and treating residue carefully above 200° C., but not high enough to decompose the sodium acetate.

Oils and Varnishes.—**510,050,** December 5, Scollay, G. W., siccatives, formed by adding to a vegetable oil a metallic oxide. **510,734,** December, 12, Trageser, A. F., apparatus for distilling and concentrating glycerol and heavy oils. **510,672,** December 12, Brown, E. G., *et al.*, "sweet residual petroleum products," purified by passing steam through petroleum while it is boiling for distillation and finally air. **511,051,** December 19, Lahusen, J. C., production of neutral wool-grease.

Plaster and Cement.—**509,924,** December 5, Lorenz, J., artificial stone, from "ashes, cinder, burnt sand and cement." **511,735,** December 26, Jones, J. K., wall plaster, sugar, 100 parts, flour, 25 parts, air-slaked lime, 250 parts, plaster of Paris, sand, and water. **510,874,** December 12, Dutrey, J., artificial emery stones, sulphur, Portland cement, emery, Venetian red and sugar form the composition. **511,740,** December 26, McIlvried, J. R., retarders for plaster, air-slaked lime is kept in an air-tight receptacle and mixed with water, flour, liquid glue, and wood ashes and dried.

Miscellaneous.—**510,421-22-23-24,** December 12, Haley, A. E., parchmentized paper board. **509,951,** December 5, Schroëder, E., manufacture of metal foil. **510,276,** December 5, Lyte, F. M., electrolysis of fused metallic chlorides in a specially devised chamber. **510,834,** December 12, Blackmore, H. S., electrolytic process for dissociating soluble salts. **510,065,** December 5, Frédureau, J. B. F., composition of matter for crockery ware, consisting of aluminum silicate combined with a soluble alkaline salt and impregnated with fatty or resinous substances. **509,887,** December 5, Fischer, J. F., and Peters, O., artificial stone filter, made by heating pulverized silica and glass to a high temperature. **510,376,** December 5, Bertrand, P. H., depositing metal upon metal by immersing in solution of soluble salts of metals in dilute sulpho-carbolic acid. **510,013,** December 5, Endruweit, C., method of producing metal film and metal paper. **511,271,** December 19, Hoskins, Wm., safety paper for checks, made by adding to paper a soluble ferrocyanide and a per-salt of iron, insoluble in water but decomposed by weak acids in presence of a soluble ferrocyanide, and a salt of manganese, decomposed by alkalies or bleaching agents.

NEW BOOKS.

DIE SCHMIERMITTEL. METHODEN ZU IHRER UNTERSUCHUNG UND WERTHBESTIMMUNG. Von Josef Grossmann, pp. 186. Wiesbaden, 1894. Price M. 4.80.

This treatise is a valuable addition to the literature of lubrication—and while no new methods are described, the bringing together of the various tests, as made use of by the German chemists, simplifies the subject and renders the book one of ready reference.

Especial attention is given to the subject of viscosity—both theoretical and practical—including the "internal resistance" of fluid lubricants. This latter subject has received but little attention in this country, and it is questionable if it is of much practical importance. Eight different viscosimeters are described, not one of which can be considered standard, showing that the same lack of uniformity in determining viscosity exists there as here.

The flash and burning tests are made in a manner similar to methods in use in our railroad laboratories, but the cold test is radically different and liable to error.

Evidently the very complete articles on this subject, by C. B. Dudley and F. N. Pease,[1] have not been consulted by the author. The tests, as formulated by Dudley and Pease, leave little to be desired in the way of accuracy and rapidity in the determination of the value of lubricants used in railroad practice.

The method for estimating rosin oil in mineral oil (Valenta's) could be supplemented by the process described by E. Twitchell, (*J. Anal. Appl. Chem.*, **5**, 379). A large portion of the treatise is devoted to descriptions of various lubricants for different kinds of machinery.

The author with many years practical experience as chief engineer of the Austrian Northwestern Railroad, gives the results of experiments in this direction, and the reasons for selecting either simple mineral oil or mixed mineral and seed-oil, for special purposes.

This portion of the work will be of value to the manufacturer of compounded oils. The treatise, while in the nature of Engineering Chemistry, is not complete enough in the qualitative reactions of the different oils and fatty acids derived therefrom to enable a chemist to accurately determine seed-oils and animal oils in the presence of each other.

If, however, Dr. Carl Schaedler's work, upon the reactions of fats and oils, be used in connection therewith, the chemist will be amply provided with the reference matter necessary on this subject. T. B. S.

[1] *The Railroad and Engineering Journal*, **6**, 76.

NOTES.

Mineral Residues in Sprayed Fruit.—Dr. R. C. Kedzie, of the Michigan Experiment Station, has examined fruit sprayed with two insecticide mixtures containing copper and arsenic. Strawberries sprayed excessively June 18 and 23 and picked June 24 contained, per pound of fruit arsenic 0.044 grains, and copper 4.87 grains. Gooseberries sprayed June 18 and 29, July 8 and 22, picked August 2, were washed with hydrochloric acid (ten per cent.) and the washed fruit contained per pound 0.0047 grains arsenic and 0.138 copper. "In these experiments extending through two years, the minerals used in spraying the fruits were found in appreciable quantities in every instance though the amount was small in all cases except where the spraying had been purposely excessive. * * * The use of poisons in horticulture in my opinion is largely in excess of the amount required for a fungicide. One-half or even one-third of the amount usually employed would probably give as good results. * * It is safe to refuse all fruits which have been sprayed with these poisons (especially arsenic) during the period of ripening."

It was found that a small part of the poison sprayed upon the surface of the fruit was absorbed into its substance.—*Bulletin, 101, Michigan Agricultural Exp't. Station, 19.*

Estimation of Chlorine in Water.—When the standard silver nitrate solution is employed, with potassium chromate as an indicator, it is often very difficult to decide just when the red color begins to appear, even with the comparison dish of water tinted with the chromate at hand as an aid to the eye. One sufficient reason therefor is that it is hard to compare a clear yellow liquid with one turbid from precipitation of silver chloride.

Following a suggestion of my assistant, Mr. V. H. Gridley, it is now my practice to roughly determine the chlorine present, and then to make a second determination using for comparison 100 cc. of distilled water to which has been added not only the chromate indicator, but also an appropriate amount of standard sodium chloride solution and an amount of silver nitrate solu-

tion just short of that necessary to satisfy the chlorine present. Of course if the chlorine ran so high as to render concentration unnecessary, then 100 cc. of the water itself with the indicator and the partial dose of silver nitrate would be the proper contents for the comparison dish. By these means the eye is greatly aided in noting the slightest appearance of red tint, for in respect of turbidity both dishes are alike. The results are very satisfactory.—*W. P. Mason, Rensselaer Polytechnic Institute, January 20, 1894.*

The Phenolsulphonic Acid Process for Nitrates in Water.—The interference of chlorides with this process, resulting in readings decidedly lower than the truth, is well known, but the method of determination is so easy and convenient, that it occurred to me to try the addition of sodium chloride to the comparison standards rather than abandon the process.

The "chlorine" in the water under examination having been previously determined, an appropriate volume of standardized sodium chloride solution is added to each evaporation of standard potassium nitrate solution. Thus the water to be examined, and the nitrate solutions with which it is compared, all contain the same quantity of chlorine. The results are very satisfactory. —*W. P. Mason, Rensselaer Polytechnic Institute, Jan. 18, 1894.*